SYNTHESIS, PHYSICO-CHEMICAL STUDIES AND CATALYTIC ACTIVITY OF GEMINI SURFACTANTS

ABSTRACT

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

BY

UMME SALMA SIDDIQUI

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

2006


Maulana Azad Library
T 660

Summary

"Surfactants", a happy and convenient contraction of "surface active agents", owe their name to their interesting behavior at surfaces and interfaces. Surfactants have a characteristic of amphipathy: the molecules have two distinct parts; one that has an affinity for the solvent and the other that does not. Hence, a surfactant can be said to have 'split personality', because it is composed of two parts of entirely different tendencies. In aqueous solutions, these two moieties are hydrophilic and hydrophobic, respectively. The amphipathic structure of the surfactant causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it. It is the tendency for the hydrophobic parts of the molecules to aggregate because of mutual dislike of the solvent which is the driving force for surfactant self-association.

Among the major incidences that happened in the world of surfactants, the most interesting is the outburst of researches on 'gemini surfactants'.[1,2] "Gemini surfactants" have structures and properties, which are different from those of monomeric surfactants and are said to be "unique to the world of surfactants". These surfactants show high surface activity, unusual viscosity changes with an increase in [surfactant], a low critical micelle

concentration (cmc), and unusual micellar structures. Geminis have already been utilized in many fields as in skin care, antibacterial regimens, construction of high porosity materials, analytical separation and solubilization process.[3-7] Also, these surfactants manifest lower critical micelle concentration (cmc), higher viscoelasticity and enhanced propensity for lowering the oil-water interfacial tension in comparison with their conventional counterparts bearing single head group and single lipophilic chain.[8,9] Micellar morphologies and properties of gemini surfactants depend strongly on the nature as well as the length of the spacer. The type of head groups in the gemini surfactants also influences their aggregation properties.

A well defined, but not abrupt, change in physical properties of surfactant solutions as one passes from a threshold value of [surfactant] is known as critical micelle concentration (cmc).[10] Near the cmc, micelles are usually spherical and the radius of the micelle is nearly equal to the length of the surfactant molecule. Upon continuous increase of concentration of the surfactant, spherical micelles become rod-shaped and subsequently these rods become hexagonally packed structures.[11]

The shape of micelles whether they are spherical or rod–like, must be ruled by a balance between the repulsive electrostatic forces of the head groups and the attractive forces that cause the aggregation. It thus seems

reasonable that the shape transition points depend on the head group including the counterion as well as the chain length of the surfactant and the location of the solubilizate in the micelles. The availability of organic additives also suppresses headgroup repulsion and promotes sphere-to-rod transition in micellar structures.[12]

Micellar solutions are known to affect the rates of chemical reactions and the positions of chemical equilibria.[13] It is generally accepted that ionic reactions occur at the micellar surface adjacent to the head groups. Rate enhancements of biomolecular reactions by aqueous micelles, or similar colloidal assemblies, are due largely to bringing together of both reactants in the small volume of the micelles. The hydrophobic and electrostatic factors play an important role in the micellar catalysis. Out of these two factors, hydrophobic effect is the most important in the organization of the constituent molecules of the living matter into complexes.

Keeping in view the importance of the novel type of surfactants, the geminis, the present thesis delves into such topics as critical micelle concentration, aggregate size and shape, and catalytic role of geminis towards ninhydrin-amino acid reactions. There are five chapters in the thesis:

In the **General Introduction (Chapter-I),** a detailed account of the behavior of surfactants, their classification, micellization, factors affecting cmc, structural transition, effect of additives on growth process and micellar catalysis are described. The importance of the research problem and an up-to-date literature survey related to the work described in subsequent chapters are also included.

Chapter-II contains the experimental details of the work. A list of chemicals used in the investigation is also included in this chapter. The main methodologies adopted are: conductance measurements, viscometric measurements, pH- measurements, dynamic light scattering measurements (DLS), spectrophotometric measurements and ^{1}H NMR measurements.

Survey of available literature reveals that no serious attempt has been made to study the micellization phenomenon of gemini surfactants in polar non-aqueous solvents. The micellization tendency of the surfactants decrease in presence of organic solvents. In **Chapter-III,** studies on the micellar properties [cmc, degree of counter ion dissociation (α), and thermodynamic parameters (ΔG^{o}_{m}, ΔH^{o}_{m}, and ΔS^{o}_{m})] of the gemini surfactants, $C_{16}H_{33}(CH_3)_2N^{+}$-$(CH_2)_s$-$N^{+}(CH_3)_2C_{16}H_{33}$, $2Br^{-}$ (s = 4, 5 or 6; 16-s-16) in water and polar nonaqueous solvent (1-propanol, PrOH; 2-methoxyethanol or methyl cellosolve, MC; dimethylsulfoxide, DMSO; acetonitrile, AN) –

water mixtures are reported. Conductometry was used to determine the cmc and α-values. The micellization of gemini surfactants occurs in many adverse situations, such as in the presence of nonaqueous solvents which are known to arrest the phenomenon of micellization. Therefore, these systems may be utilized for the organic reactions which are occurring in polar solvents or in the presence of binary solvents whose one component is water.

A vast majority of experimental data are available on solution/aggregational behavior of conventional surfactants in presence of different classes of additives. Most studies on geminis are related to their specific aggregation behavior and structural properties[14-16] but morphological studies of geminis in the presence of different class of additives has not been systematically investigated. Being an entirely a new field of research, viscometric and dynamic light scattering (DLS) measurements have been performed on the dimeric gemini surfactants to see the role of organic additives (alcohols; C_4-C_6OH and hexylamine; C_6NH_2) in the absence and presence of KBr towards micellar growth. With respect to the corresponding monomeric surfactant cetyltrimethylammonium bromide (CTAB), dimeric surfactants have been found to have a much stronger tendency for micellar growth. The results are described in **Chapter-IV**. The addition of a general ionic salt KBr plays a role in weakening electrostatic repulsions between the

gemini micelle cationic headgroups and thereby induces structural changes from spherical to rod-like or disK-like shape. The presence of primary alcohols (butanol, pentanol, hexanol) enhances the sphere-to-rod transition and reduces the threshold concentration for the onset. This is due to the formation of the gemini-alcohol mixed micelles. Thus, the micellar size is larger in presence of alcohols as confirmed by the applied techniques.The alcohols progressively get embedded between the monomers of the micelle, which increases the volume of the micellar core. Thus, longer alkyl chain alcohols form efficiently larger micelles. A combined presence of KBr and alcohols or *n*-hexylamine shows a synergistic effect, which produce favorable conditions for micellar growth which do not exist in presence of either the salt or additive alone. For additives of equal chain length of alcohol and amine (C_6OH and C_6NH_2), the alcohol is found more effective for cationic gemini micellar growth.

The use of ninhydrin for the detection and estimation of amino acids has been the subject of various investigations because of its potential ability to reveal latent fingerprints.[17] The use depends on the formation of a purple-colored product (*Ruhemann's purple*) whose amount depends upon reaction conditions, i.e., pH, temperature, reactant concentrations, etc.[18] The technique, although useful, still has room for improvements. With the view

that the method could find applications to improve contrast and visualization of ninhydrin-developed fingerprints and may prove a step forward from the methods already used in current forensic research, systematic kinetic studies were performed of the ninhydrin-L-isoleucine reaction in the presence of micellar media. Due to improved performance of geminis on almost all fronts for which conventional surfactants are utilized, effects of three synthesized geminis on the rate of ninhydrin-L-isoleucine reaction were studied in detail. Optimum conditions can be obtained by studying the effect of various factors (pH, [L-isoleucine], [ninhydrin], solvents) on the rate and extent of the reaction. The following conclusions are made regarding the catalytic effect of the gemini micelles (16-*s*-16, s = 4, 5, 6) on the ninhydrin L–isoleucine reaction, investigated at pH = 5 and 80 °C: Dicationic gemini micelles provide much better environment for ninhydrin-L-isoleucine reaction as compared to their corresponding monocationic counterpart CTAB micelles. It is known that the spacer chain at headgroup level of geminis decrease the extent of water penetration at the micellar surface: this could be the reason of kinetic advantages of the geminis used in the present studies. In addition to typical rate constant increase and leveling-off regions (just like conventional CTAB), an unusual third region of increasing k_ψ at [16-*s*-16]≥ 60xcmc was observed. ^{1}H NMR studies reveal the formation of

larger aggregates at these higher surfactant concentrations which provide less polar environment and hence k_ψ increases. Based on the above, the ninhydrin-L-isoleucine reaction can thus be used as a simple and reliable kinetic probe in aggregate structures. The catalyzing effect of organic solvents (1-propanol, methyl cellosolve, acetonitrile, dimethylsulfoxide) seems due to the blockage of side reaction(s) and higher solubility of the product.

References

1. F. M. Menger and J. S. Kieper, *Angew. Chem. Int. Ed.*, **39**, 1906 (2000).
2. R. Zana, *Adv. Colloid Interface Sci.*, **97**, 205 (2002).
3. P. V. D. Voort, M. Mathieu, F. Mees and E. F. Vansant, *J. Phys. Chem. B*, **102**, 8847 (1998).
4. K. Chen, D. C. Locke, T. Maldacker, J. L. Lin, S. Aawasiripong and U. Schurrath, *J. Chromatogr. A*, **822**, 281 (1998).
5. M. Dreja and B. Tieke, *Langmuir*, **14**, 800 (1998).
6. F. Li and M. J. Rosen, *J. Colloid Interface Sci.*, **224**, 265 (2000).
7. M. Pavilikova, I. Lacko, F. Devinsky and D. Nlynarak, *Collect. Czech. Chem. Commun.*, **60**, 1213 (1995).
8. F. M. Menger and C.A. Littau, *J. Am. Chem. Soc.*, **113**, 1451 (1991).
9. R. Zana and Y. Talmon, *Nature* **362**, 228 (1993).
10. D. J. Shaw, "*Introduction to Colloid and Surface Chemistry*" : 2nd ed., Butterworths, London (1970).
11. J. N. Israelachvili, "*Intermolecular and Surface Forces*" : 2nd ed., Academic, London (1991).
12. E. Caponetti, D. C. Martino, M. A. Floriano and R. Trilo, *Langmuir*, **13**, 3277 (1997).

13.(a) T. Kunitake and T. Shinkai, *Adv. Phys. Org. Chem.*, **17**, 435 (1980). (b) J. H. Fendler, "*Membrane Mimetic Chemistry*", Wiley, New York (1981). (c) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, **22**, 213 (1986). (d) C. A. Bunton, F. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res.*, **24**, 357 (1991). (e) L. S. Romsted, C. A. Bunton and J. Yao, *Curr. Opin. Colloid Interface Sci.*, **2**, 622 (1997). (f) O. A. El Seoud, *Adv. Colloid Interface Sci.*, **30**, 1 (1989). (g) S. Tascioglu, *Tetrahedron*, **34**, 11113 (1996).

14. F. Devinsky, I. Lacko and T. Imam, *J. Colloid Inerface Sci.*, **143**, 336 (1993).

15. Th. Dam, J. B. F. N. Engberts, J. Karthauser, S. Karaborni and N. M. Van Os, *Colloids Surf. A.*, **118**, 41 (1996).

16. E. Buhler, E. Mendes, P. Boltenhagen, J. P. Munch, R. Zana and S. J. Candau, *Langmuir,* **13**, 3096 (1997).

17 (a) M. M. Joullie, T. R. Thompson and N. H. Nemeroff, *Tetrahedron*, **47**, 8791 (1991). (b) S. Oden and B. Von Hofsten, *Nature*, **173**, 449 (1954). (c) J. Almog, in "*Advances in Fingerprint Technology*", Edited by H. Lee and R. E. Gaensslen, Elseveir Science, New York (1991).

18. (a) Z. Khan and A. A. Khan, *J. Indian Chem. Soc.*, **66**, 454 (1989).

(b) Z. Khan and A. A. Khan, *J. Indian Chem. Soc.*, **67**, 963 (1990).

(c) Z. Khan, D. Gupta and A. A. Khan, *Int. J. Chem. Kinet.*, **24**, 481 (1992).

SYNTHESIS, PHYSICO-CHEMICAL STUDIES AND CATALYTIC ACTIVITY OF GEMINI SURFACTANTS

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

BY

UMME SALMA SIDDIQUI

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

2006

Dedicated

to

My loving Mummy and Papa

PROF. KABIR-UD-DIN
DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH-202002
(U. P.) INDIA.
E-mail: kabir7@rediffmail.com

☎ (0571) –2703515 (O)
(0571) -2700920
Exnt. 3353 (Lab), 3351 (O)

Dated: Dec. 12, 2006

Certificate

This is to certify that the thesis entitled **"Synthesis, Physico-Chemical Studies and Catalytic Activity of Gemini Surfactants"** is the original work carried out by **Ms. Umme Salma Siddiqui** under my supervision and is suitable for submission for the award of **Ph.D.** degree in **Chemistry**.

(Prof. Kabir-ud-Din)

Acknowledgement

I wish to express my gratitude to all the people involved in the writing of this thesis.

Words are inadequate to express my gratitude to ***Prof. Kabir-ud-Din****, my supervisor and guide, for his guidance, intellectual stimulations and helping hand during my tenure under him for this endeavour.*

I wish to gratefully acknowledge ***Dr. Sanjeev Kumar*** *(Lecturer, M. S. University, Vadodara), who was very generous in sharing his time and knowledge with me and also* ***Dr. Zaheer Khan*** *(Reader, Jamia Millia Islamia, New Delhi) for his timely help.*

Thanks are due to my seniors ***Dr. M. Akram, Dr. Andleeb Zehra Naqvi*** *and* ***Dr. Ziya Ahmad Khan,*** *for their tips and timely suggestions.*

I must mention with profound gratitude the support and friendly attitude of my lab colleagues ***Mr. S. M. Shakeel Iqubal, Dr. Sajid Ali, Ms. Waseefa Fatma, Ms. Deepti Sharma, Ms. Nuzhat Gull, Md. Sayem Alam, Mr. Tanweer Ahmad, Ms. Neelam Hazoor Zaidi, Mr. Naved Azum, Mr. Md. Altaf, Ms. Suraiya Khatoon, Mr. Md. Dabi Ali Al Ahmadi, Mr. Riyaz Mohammad and Mr. Mohmad Shafi*** *for creating friendly atmosphere to work in and all time support.*

It has been a pleasure to work with ***Dr. Goutam Ghosh****, Bhabha Atomic Research Center, Mumbai, and his cooperation is much appreciated. I am also very grateful to* ***Dr. P. S. Goyal****, Center Director, UGC-DAE CSR, BARC, Mumbai, for allowing me to perform DLS measurements.*

Special words of thanks to ***Prof. Wajid H. Ansari****, Department of Chemistry, for his valuable suggestions and generous help.*

I am also thankful to my husband ***Mr. Ashiq Hussain*** *for his patience and cooperation during this period.*

My sincere thanks go to my in-laws for their gentle support.

I heartly mention my friends, ***Ms. Rabia Khanam, Ms. Nikhat Afreen, Ms. Sana, Mr. Asad Mohd. Khan*** *and* ***Mr. Salman Shamshad*** *who have selflessly enriched me beyond measure. I thank them all.*

I pay special thanks to my room mate and my friend ***Ms. Shaista Ahmad*** *for her all time emotional support in my all ups and downs.*

My deepest gratitude to my mother ***Mrs. Talat Waseem****, my father* ***Mr. W. H. Siddiqui*** *and my sisters* ***Ms. Samira Siddiqui, Ms. Nazia Siddiqui, Ms. Farheena Siddiqui*** *for their unfailing emotional support during the entire period.*

I am thankful to my alter ego ***Ms. Ghazala Hassan*** *for her unspoken support during this period.*

At last I want to appreciate ***Mr.Bilal Akhtar (Goldi)*** *for his hard work during my typing.*

(Umme Salma Siddiqui)

List of Publications

1. Effect of Cationic CTAB Micelles on the L-Isoleucine – Ninhydrin Reaction.
   Kabir-ud-Din, **Umme Salma Siddiqui** and Z. Khan
   J. Surface Sci. Technol. (India), **19**, 101-116 (2003).

2. Micellization of Monomeric and Dimeric (Gemini) Surfactants in Polar Nonaqueous – Water Mixed Solvents.
   Kabir-ud-Din, **Umme Salma Siddiqui**, Sanjeev Kumar and Aijaz Ahmad Dar
   Colloid Polym. Sci. (U.K.), **284**, 807-812 (2006).

3. DLS Studies of Additive Effects on the Microstructure of Aqueous Gemini Micelles.
   Umme Salma Siddiqui, Goutam Ghosh and Kabir-ud-Din
   Langmuir (U.S.A.), **22**, 9874-9878 (2006).

4. Viscometric Studies on Aqueous Gemini Micelles in the Presence of Additives.
   Kabir-ud-Din, **Umme Salma Siddiqui** and Sanjeev Kumar
   Colloids Surf. A: Physicochem. Eng. Aspects (The Netherlands), (communicated).

5. Catalytic Role of Gemini Surfactant Micelles in the Ninhydrin – L-Isoleucine Reaction.
   Umme Salma Siddiqui and Kabir-ud-Din
   J. Colloid Interface Sci. (U. S. A.), (communicated).

6. Growth of Gemini Micelles in the Presence of Additives: Viscometric and DLS Studies.
   Umme Salma Siddiqui, Goutam Ghosh and Kabir-ud-Din
   Langmuir (U. S. A), (communicated).

List of Papers Presented/Accepted At Conferences

1. Effect of Cationic CTAB Micelles on the L-Isoleucine–Ninhydrin Reaction.
   Kabir-ud-Din, **Umme Salma Siddiqui** and Zaheer Khan
   11th National Conference on Surfactants, Emulsions and Biocolloids, Mumbai, Dec. 11 - 13, 2003, A 118.

2. Micellization of Monomeric and Dimeric (Gemini) Surfactants in Polar Non-aqueous-Water Mixed Solvents.
   Kabir-ud-Din, **Umme Salma Siddiqui** and Sanjeev Kumar
   International Conference on Soft Matter, Kolkata, Nov. 18-20, 2004, P 31, p. 91.

3. Structural Studies on Gemini Micelles.
   Kabir-ud-Din, Waseefa Fatma, **Umme Salma Siddiqui** and Sanjeev Kumar
   7th CRSI National Symposium in Chemistry, Indian Association for the Cultivation of Science, Kolkata, Feb. 4-6, 2005, P 275, p. 297.

4. Viscometric Studies on Aqueous Dimeric Surfactants in the Presence of Additives.
   Kabir-ud-Din and **Umme Salma Siddiqui**
   16th International Symposium on Surfactants in Solution (SIS 2006), Seoul (Korea), June 4-9, 2006, OW16, p. 140.

5. Additive Effects on the Morphology of Aqueous Gemini Micelles.
   Kabir-ud-Din and **Umme Salma Siddiqui**
   National Conference on Disperse Systems, Assam University, Silchar, Nov. 23-25, 2006.

Contents

Chapter-I

General Introduction

Surfactants and Surfactant Micelles

"Surfactants", a happy and convenient contraction of "surface active agents", owe their name to their interesting behavior at surfaces and interfaces. When present at low concentration in a system, they have the property of adsorbing onto the surfaces or interfaces of the system and the adsorption of surfactant lowers the interfacial tension between phases. Because of their ability to lower interfacial tension, surfactants are used as emulsifiers, detergents, dispersing agents, foaming agents, wetting agents, penetrating agents and so forth.

Surfactants have a characteristic of amphipathy: the molecules have two distinct parts; one that has an affinity for the solvent and the other that does not. Hence, a surfactant can be said to have 'split personality', because it is composed of two parts of entirely different tendencies. In aqueous solutions, these two moieties are hydrophilic and hydrophobic, respectively. Often the hydrophilic part of the molecule is simply called the 'head' and the hydrophobic part– usually including an elongated alkyl substituent– is called the 'tail'. The amphipathic structure of the surfactant causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with

its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it. It is the tendency for the hydrophobic parts of the molecules to aggregate because of mutual dislike of the solvent which is the driving force for surfactant self-association.

The chemical structures of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. In a highly polar solvent such as water, the lyophobic group may be a hydrocarbon or fluorocarbon or siloxane chain of proper length, whereas in less polar solvent only some of these may be suitable (e.g., fluorocarbon or siloxane chains in polypropylene glycol). In a polar solvent such as water, ionic or highly polar groups may act as lyophilic groups, whereas in a nonpolar solvent such as heptane they may act as lyophobic groups. As the temperature and use conditions (e.g., presence of electrolyte or organic additives) vary, modifications in the structure of the lyophobic and lyophilic groups may become necessary to maintain surface activity at a suitable level. Thus, for surface activity in a particular system the surfactant molecule must have a chemical structure that is amphipathic in that solvent under the conditions of use.

Classification of Surfactants: Surfactants are classified on the basis of the charge carried by the polar head group as:

Anionic. The surface-active portion of the molecule bears a negative charge, for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

Cationic. The surface-active portion bears a positive charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).

Zwitterionic. Both positive and negative charges may be present in the surface-active portion, for example, $RN^+H_3CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).

Nonionic. The surface-active portion bears no apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

Gemini. Gemini[1,2] surfactants are defined as surfactants made up of two identical amphiphilic moieties connected at the level of the head groups, by a spacer group which can be hydrophilic or hydrophobic, rigid or flexible (Fig. 2).[3] Thus, an ionic gemini has in sequence a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail.

A schematic representation of gemini is given in Fig. 1.1.

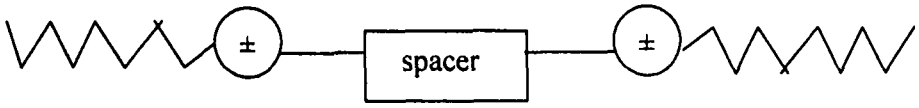


Fig. 1.1. Schematic representation of gemini surfactants.

Geminis were known long before to Bunton et al.,[4] who studied the catalysis of nucleophilic substitutions by "dicationic detergents", to Devinsky et al.,[5] who reported on the surface activity and micelle formation of some new "bisquaternary ammonium salts", and to Okahara et al.,[6] who prepared and examined "amphipathic compounds with two sulphate groups and two lipophilic alkyl chains". Later in 1991, Menger and Littau[1] assigned the name "gemini" to bis-surfactants with rigid spacer (i.e., benzene, stillbene).

Geminis can have unusual and exceptional structural features. The relevant structure features include:

(a) All geminis possess at least two hydrophobic chains and two ionic or polar groups.

(b) A great deal of variation exists in the nature of the spacer, which can be short (2 methylene groups) or long (12 methylene groups); rigid (stillbene) or flexible (methylene chain); and polar (polyether) or nonpolar (aliphatic, aromatic).

(c) The polar group can be positive (ammonium), negative (phosphate, sulfate, carboxylate), or nonionic (polyether, sugar). [7]

(d) Although the great majority of geminis have two identical polar groups and two identical chains, unsymmetric geminis are known.[8,9]

(e) "Geminis" with three or more polar groups or tails have been synthesized.[10-12]

Gemini surfactants attract current attention in the area of surfactant science because of the number of unique properties that they manifest. For instance, they have been used in various purposes such as the preparation of high porosity materials, analytical separations, solubilization processes, skin care formulations, antibacterial regimens, and anti-pollution protocols.[13-17] Also, these surfactants manifest lower critical micelle concentration (cmc), higher viscoelasticity and enhanced propensity for lowering the oil-water interfacial tension in comparison with their conventional counterparts bearing single head group and single lipophilic chain.[1,18] Micellar morphologies and properties of gemini surfactants depend strongly on the nature as well as the length of the spacer. The type of headgroups in the gemini surfactants also influences their aggregation properties.

Thus, keeping in view the importance of these novel type of surfactants, the geminis, this thesis delves into such topics as critical micelle

concentration, aggregate size and shape, and catalytic role of geminis towards ninhydrin-amino acid reactions.

Micelle Formation: One of the most characteristic properties of amphiphilic molecules is their capacity to aggregate in solutions. The aggregation process depends of course, on the amphiphilic species and the condition of the system in which they are dissolved. The narrow concentration range over which surfactant solutions show an abrupt change (Fig. 1.2) in physicochemical properties is called the critical concentration for the formation of micelle or 'critical micelle concentration' (cmc).[19-21] cmc values for commonly used surfactants range from about 10^{-4} to 10^{-2} M. [22,23] Term cmc was established by Bury,[24] defining it as a concentration range below which surfactant is in solution as monomer and above which practically all additional surfactant added to the solution forms micelles. Just above the cmc, micellar structure is considered to be roughly globular or spherical. [22,23] A schematic representation of such a structure is given in Fig. 1.3. However, the exact structure of micelles is still somewhat controversial. There is evidence, for example, that micelles have a rough surface with considerable penetration of water between head groups.[23]

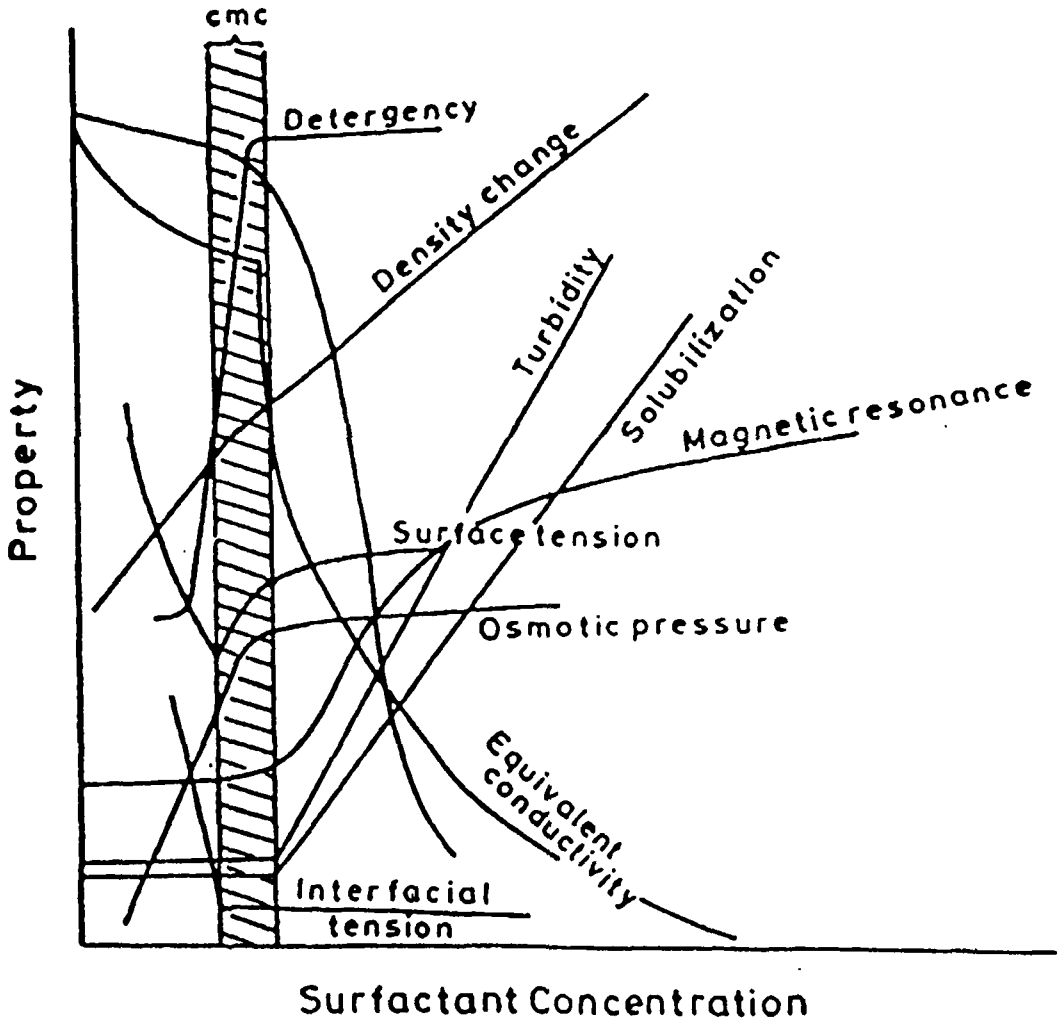


Fig.1.2. Variation of physical properties with surfactant concentrations.

Although an oversimplification, Fig. 1.3 is a useful model for qualitative understanding of experimental results. Hydrophobic cores of micelles have diameters of about 10-30 Å. The charged coat of ionic micelles, called the Stern layer, is usually 60-90% neutralized by counterions in aqueous surfactant solutions without added salt.[23] The surface charge of ionic micelles results in an electrical potential on the order of 100mV at the micellar-water interface with the same sign as the surfactant head group.[25] If salt is added to the solution, the surface potential is partly neutralized. This decreases coulombic repulsion between adjacent head groups and allows the formation of larger micelles. A solution having a single, very narrow, distribution of micellar sizes is often called monodisperse.

As concentrations of surfactant or salt (or both) in water are increased, globular micelles gradually turn into larger, rodlike micelles. Under some experimental conditions, spherical and rodlike micelles coexist in the same solution. Systems containing two distinct distributions of micellar sizes are called polydisperse. At higher concentrations of surfactant or salt, rodlike micelles begin to predominate. Finally, at very high surfactant concentrations, lamellar liquid crystal phases may be formed.[23]

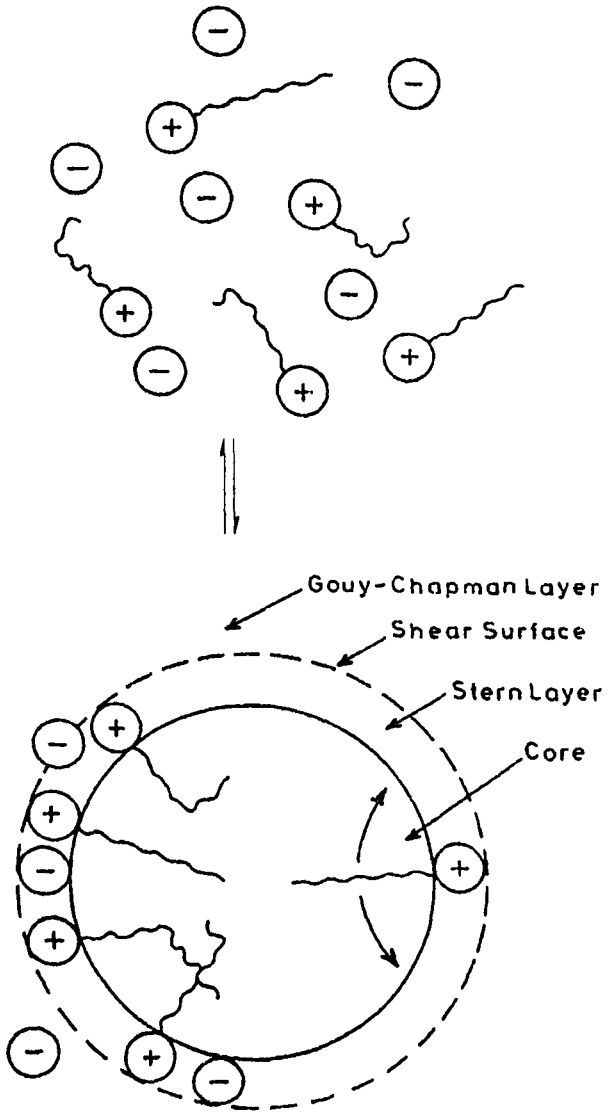


Fig. 1.3. Model of hypothetical ionic micelle showing the locations of headgroups, surfactant chains and counterions. Curved arrows symbolize the liquid – hydrocarbon – like nature of the core.

Not all surfactants form micelles in water. Depending on structure, some surfactants disperse in water as lamellar liquid crystal phases or vesicles. The practical result is that water-soluble, single chain surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium bromide, and polyoxyethylene alcohols form micelles in water. Double-chain surfactants such as didodecyldimethylammonium bromide, dihexadecylphosphate, and many phospholipids are insoluble in water and do not form micellar structures.

Micellization Parameters

Critical micelle concentration, aggregation number, counterion binding constant, free energy of micellization, etc., are the main micellization parameters. There have been various physico-chemical studies made on micellar solutions for determining these parameters. Among all these micellization parameters cmc is the most significant parameter which has been widely studied and discussed.

Critical Micelle Concentration: Many investigators have developed empirical equations relating to cmc to the various structural units in surfactants. Thus, for homologous straight chain ionic surfactants (soaps, alkane sulfonates, alkyl sulfates, alkylammonium chlorides, alkyltrimethylammonium halides) in aqueous medium, a relationship

between the cmc and the number of carbon atoms n in the hydrophobic chain was found as

$$\log C_{cmc} = a - bn \qquad (1.1)$$

where a is a constant for a particular ionic head at given temperature and b is a constant = 0.3 (= log 2) at 35 °C, for the ionic types mentioned above.

The aggregation of monomers to micelles results in a free energy decrease. When micelles are formed, the high energy of the hydrocarbon/water interface is lost, as the chain is now in contact with others of a like nature. Also, the structure of the water around the hydrocarbon part of the monomer is lost. Hence, due to this disorder with respect to water, a positive entropy change and simultaneously a decrease in free energy occurs. Thus, the loss of hydrocarbon/water interfacial energy and loss of water structure are the driving forces for the formation of micelles.

The two most important techniques which are used for determining cmc values are surface tension and solubilization, i.e., the solubility of an otherwise insoluble compound. For an ionic surfactant, the cmc can be obtained easily by conductivity. However as, a very large number of physico-chemical properties are sensitive to surfactant micellization, there are various other techniques, such as self–diffusion measurement, nuclear

magnetic resonance, fluorescence spectroscopy, etc. In case of long–chain surfactants an accurate determination of cmc is straightforward and different techniques give the same results. However, for short–chain, weakly associating surfactants, this is not the case and rather greater care is required not only in the measurements but also in evaluating the cmc from experimental data.

Factors Affecting the Value of Critical Micelle Concentration: When the micelle formation takes place, the properties of solutions of surface-active agents change markedly. Following are the main factors that are found to affect the cmc in aqueous solutions: (i) structure of the surfactant, (ii) the presence of added electrolyte in the solution, (iii) the presence of various organic additives in the solution, (iv) the temperature of the solution, (v) pressure, and (vi) solvents.

(a) ***Structure of surfactant.*** In general, the cmc decreases as the hydrophobic character of the surfactant increases, i.e., cmc decreases as the number of the carbon atoms in the hydrophobic group increases (see Eq. 1.1). In aqueous medium ionic surfactants have much higher cmc's than non-ionic surfactants containing equivalent groups. Zwitterionic surfactants appear to have about the same cmc's as ionics with the same number of carbon atoms in hydrophobic group. The

cmc increases as the head group is closer to the two branches of the chain partially shielding one another, interfacial energy effects are smallest. In aqueous medium, the cmc's of ionic surfactants decrease with decrease in the hydrated radius of the counterion.

(b) ***Effect of electrolyte addition.*** In aqueous solution of ionic surfactant the presence of electrolyte causes a decrease in the cmc. On increasing electrolyte concentration, the forces of electrostatic repulsion between headgroups in a micelle are considerably reduced, enabling micelles to form more easily, i.e., at lower concentration. The order of effectiveness of added electrolytes containing different counterions in decreasing the cmc[26,27] is $^{1/2}SO4^{-2} > F^- > BrO_3^- > Cl^- > Br^- > NO_3^- > I^- > CNS^-$ and $NH_4^+ > K^+ > Na^+ > Li^+ > {}^{1/2}Ca^{+2}$.

(c) ***Organic additives.*** Organic compounds affect the cmc either by penetrating into the micellar region, or by modifying solvent-micelle or solvent-monomer interactions. Non-polar compounds, such as hydrocarbons, that are believed to penetrate into the inner portion of the core, decrease the cmc only slightly. Addition of longer chain alcohols promotes micelle formation and lowers the cmc. The magnitude of cmc decrease depends on the alkyl chain length of the organic additive and the hydrophilic group associated with the chain.

Urea, formamide, and guanidium salts are believed to increase the cmc of surfactants in aqueous solution because of their disruption of the water structure. These water structure breakers may also increase the cmc by increasing the entropy effect accompanying micellization.

Materials that promote water structure (carbohydrates), for similar reasons, decrease the cmc of the surfactant.

(d) ***Temperature.*** The effect of temperature on micelle formation is essentially guided by the way temperature affects the solubility and other behaviors of surfactants in solution. Temperature increase causes decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also causes the disruption of the "structured water" surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposite effects, therefore, determines whether the cmc increases or decreases over a particular temperature range.

The thermodynamic parameters (free energy change, enthalpy and entropy) can also be calculated from cmc.

(e) ***Pressure.*** Many reports have appeared on the effect of pressure on micelle formation of the ionic [28-30] and nonionic surfactants[31]. With

pressure cmc of ionic surfactants increases upto 1000 atm followed by a decrease above this pressure.[32-34] Such behavior has been rationalized in terms of solidification of the micellar interior,[32] increased dielectric constant of water[35], and other aspects related to water structure.[36] For nonionic surfactants, the cmc value increases monotonously and then levels off with increasing pressure.

(f) ***Polar nonaqueous solvents***. For micelle formation in polar non aqueous solvents, the term "solvophobic interaction" has been coined, in analogy with "hydrophobic interactions"' which causes micellization in aqueous medium.[21] The micelles formed due to "solvophobic interactions" are similar in many respects to the micelles that are formed in aqueous medium, although in general, micelle formation is not as favored in nonaqueous solvents as in water for a given surfactant.[37]

Aggregation Number: The micelle aggregation number (n_s) which is the number of surfactant monomers or dimers making up a micelle, is affected by different factors such as the nature of the surfactant, temperature,[38] type and concentration of added electrolyte,[39] organic additives, etc. The value of the aggregation number contains information on the micelle size and shape, which may be important in determining the stability and the practical

applications of the investigated systems.[40,41] Many methods have been used to determine micelle aggregation numbers like quasi-elastic light scattering, small–angle–neutron scattering,[42] steady-state fluorescence quenching[43] and time-resolved fluorescence quenching.[44]

In aqueous medium, the greater the 'dissimilarity' between surfactant and solvent, the greater the aggregation number. An increase in the temperature appears to cause a decrease in the aggregation number of the ionic surfactants.[38,45,46] For non-ionic surfactants, it increases fairly rapidly.[47]

Structural Transition in Micellar Solutions

Amphiphilic substances are capable of forming supramolecular systems,[48] from thermotropic-lyotropic liquid crystals and manifold micellar systems upto the highly ordered membranes in liposomes and cells. At low surfactant concentration, first above the cmc, micelles are usually spherical,[49] while at higher concentrations they assume rod– or disk like shapes.[50] Micelles transform to lyotropic liquid crystalline structures[51] at very high surfactant concentrations.

Not only overall surfactant concentration, but varying other solution conditions such as, surfactant composition, additives in the liquid phase, temperature, pressure, ionic strength and pH[40] are also known to promote structural transition.

The shape of micelles whether they are spherical or rod–like, must be ruled by a balance between the repulsive electrostatic forces of the head groups and the attractive forces that cause the aggregation. It thus seems reasonable that the shape transition points depend on the head group including the counterion as well as the chain length of the surfactant and the location of the solubilizate in the micelles.

The shape and size of these micellar aggregates can, in principle, be determined by various methods, such as viscosity,[52] small–angle–neutron scattering (SANS),[53] light scattering,[54-56] ultrasonic absorption[57], time–resolved fluorescence,[58,59] etc.

Growth of the aggregates has been observed by light scattering; [60-63] viscosity,[64-68] flow birefringence measurements,[69] SANS,[70-72] and by Cryo-TEM.[73,74]

Packing Parameter: The shape of micelles depends strongly upon the actual packing parameters in micellar assembly.[75-77] The surfactant packing parameter, introduced by by Israelachvili *et al.*[78] provides an empirical criterion for predicting the shape that the aggregates of a given surfactant will adopt in aqueous solutions. The packing parameter, R_p is given by: $R_p = v/a.l$ where v is the volume occupied by the hydrophobic moiety of the amphiphilic molecule, l is the critical length in the fully extended

conformation and a is the optimal cross section surface area occupied by an amphiphilic headgroup at the water-aggregate interface. Both l and v can be calculated for a saturated hydrocarbon chain of n carbon atoms using Tanford's equations.[79]

$$l = (1.5 + 1.265\ n)\ \text{Å}, \qquad (1.2)$$

$$v = (27.4 + 26.9\ n)\ \text{Å}^3, \qquad (1.3)$$

Specific values of R_p are associated with spherical micelles ($R_p < 0.33$), worm-like micelles ($0.33 < R_p < 1$), flat bilayers ($R_p = 1$), and inverted micelles ($R_p > 1$). The factors that influence the mobility of the hydrophobic chains and the hydration of the headgroup, e.g., unsaturation in the hydrophobic tail, pH, temperature and the presence of the electrolytes may affect the R_p -value.

Effect of Additives on Growth Process:

(a) ***Effect of salts.*** For concentrated surfactant solutions, the inorganic salts are used as thickening agents. The effects of inorganic salts on ionic surfactant solutions have been discussed in terms of electrostatic interactions, changes in the structure of water, ionic hydratability, etc.[77,80-83] The repulsive force between the head groups is decreased by the presence of salt ions near the polar heads of the surfactant molecules. Due to this reduction in the repulsion, the surfactant molecules approach each other

more closely and as a result larger aggregates are formed which require much more space for the hydrophobic chains. The two main factors which are responsible for structural transition in presence of salts are – (a) electrostatic effect of simple salts due to the counterion binding on ionic micelles, (b) hydrophobic interaction between surfactant molecules or ions caused by the change in the hydrogen–bonded structure of water. It has been reported that the micellar sphere-to-rod transition is highly dependent upon the nature of the counterions. The micellar transition is promoted by the strong counterion binding, which can be shown by higher increase in the relative viscosities.[67,69,84-92] The salt-induced formation of rod-like micelles in aqueous salt solutions has been reported for a series of cationic surfactants[63,93-105] by different techniques such as light scattering,[95,97,102] flow birefringence,[101,103] viscosity,[95] solubilzation,[96,100] ^{1}H NMR,[98] SANS,[99,105] and electron microscopy.[104]

Counterions are 'bound' primarily by the strong electrical field created by the head groups but also by specific interactions that depend upon head groups and counterion type. Micellar shapes should be determined under experimental conditions because the shape of the micelles are sensitive to surfactant chain-length, structure of the head group and type of thecounterion.[1,20,106-108]

Specific counterion effects on a variety of micellar shapes generally follow a Hofmeister series,[1] i.e., for counterions of the same valence, the size of the micelle increases with size of the counterion (crystal radius) and the ease of dehydration of counterion.[109-112] However, sphericity may also depend upon the interactions of hydrogen bonding between hydrated counterions and head groups and counterions, and the possibility that a fraction of the counterions are sitebound to surfactant headgroup, e.g., contact ion-pair formation cannot be ignored.

Double tailed amphiphiles usually form bilayer sheets, as their most hydrated state allows the molecules to pack only in a lamellar arrangement. When bilayer sheets are closed, vesicles are formed.[113-115] Lamellar aggregates are also formed from the mixtures of anionic and cationic surfactants in water[116] or mixtures of ionic surfactants and long-chain alcohols in water[118] or electrolyte solution.[118] Some surfactant molecules in aqueous solution are spontaneously transformed from micelles into a lamellar array in the presence of a high salt concentration. This morphological change is facilitated by an increase in counterion binding and dehydration of the surfactant head groups and bound counterions. This salt-induced lamellar arrangement of surfactant molecules is commercially utilized in liquid laundry detergents.[119-122]

(b) ***Effect of organic additives.*** The effect of organic additives on the micellar size and shape has been explained in terms of their effects on water structure and on their role inside the micelle. Aqueous micellar solutions are known to solubilize water insoluble or slightly soluble organic compounds. It has been suggested that the short chain alcohols are localized mainly in the aqueous phase, which therefore changes the micellar structure by altering the organization of solvent molecules. Medium chain length alcohols are distributed between the two phases (i.e., micelle and bulk water) and long chain length alcohols are localized in the micellar phase.[123,124]

At the air-water interface,[125] amines are more surface active than alcohols. Due to electrostatic and hydrophobic effects, C_4-C_{10} *n*-alkyl amines are solubilized in micelles and the amine group is left at the micellar surface.[126]

On the basis of their hydrophilicity three different classes of additives were ranked by Wormuth et al.[127] Primary amines were found more hydrophilic than either alcohols or carboxylic acids. But when coupled with anionic surfactant the hydrophilicity of amine was lower than expected. On comparison, amines have been found to be more effective in SDS than in TTAB as observed by Lindemuth and Betrand.[128] This is due to the interaction between the amines and the anionic surfactant headgroup at the

micellar interface. Besides this, amine head group has the ability to reside deeper in the SDS micelle, which relieves the requirement of the tails of the surfactant to reach the center of the micelle at a shorter alkyl chain length of additive. In case of interaction of cationic surfactants with carboxylic acids similar effects were seen. Thus, a cosurfactant with the ability to bear an opposite charge to that of the surfactant headgroup, is more effective at promoting sphere-to-rod transition and has the ability to better penetrate the surfactant rich film, separating the micellar and aqueous pseudophases.[129] Similar effect was seen by Prasad and Singh[130] in case of SDS and CTAB micelles.

It is well known that to maintain a spherical form, the micellar tails must be reachable to the center of the micelle. On addition, an aliphatic hydrocarbon generally resides in the micellar core. Now the association structure can maintain spherical form containing the solubilized oil at a radius which was previously prohibitive. In this way the presence of aliphatic hydrocarbons retard the structural transition.

On the other hand, the presence of aromatic hydrocarbons stimulate rod growth in case of cationic surfactants, which may rise from the interaction of the delocalized π-electron cloud of the benzene ring with the positive charges of the surfactant head groups; a behavior very similar to

that of a cosurfactant or counterion. The resulting reduction of head group repulsion favors transition to rods by shrinking the surface area occupied per amphiphile, thus increasing the aggregation number.

(c) ***Synergistic effect of salts + organics.*** Kabir-ud-Din and coworkers[131-137] reported that the combined presence of salts and organic additives produces a synergistic effect (e.g., significant increase in viscosity) in micellar solutions. This synergism is dependent on the nature of the additives. It was also found that the presence of salt may change the conventional solubilization site of a particular additive and thus produce different micellar morphologies.

The effect of addition of *n*-alcohols on the viscosity of CTAB[138] was studied by capillary viscometry method. Prasad and Singh found that the lower alcohols (C_2 and C_3OH) decreased the viscosity of CTAB solution in presence of 0.1 M KBr right from the beginning, while C_4, C_5 and C_6OH in low concentration were found to increase the viscosities. Depending on the nature of the alcohol, further addition made the solution either turbid or lowered the viscosity of the solution. The result was interpreted in terms of the possible micellar transition from rod to sphere or elongated rods in presence of added alcohols. It is known that rod-shaped micelles are formed in aqueous solutions of 0.1M CTAB + 0.1 M KBr.[139] The effects of added

aliphatic *n*-amines (C_4, C_6, C_7 or C_8NH_2) and temperature on the above system show that transition of rod-shaped micelles to larger aggregates is induced by addition of higher amines ($>C_6NH_2$) and that too upto a certain concentration only: a further increase in concentration produced the opposite effect. Addition of C_4NH_2 amine was reported to induce only a rod-to-sphere transition. Kumar et al,[140] interpreted the data in terms of solubilization/ incorporation (decrease of micellar surface charge density) of amines inside in the micelles and nature of the effective solvent (water + amine). The latter effect dominated the change from larger aggregates to smaller micelles at higher concentrations of the added amine.

Micellar catalysis

Most important reactions occur not in a homogenous solution but at an interface. Many industrially important processes occur on the surfaces of solid catalysts, and nearly all biological reactions take place at gas-liquid interfaces or on an enzyme that may itself be bound to a membrane. The properties of these catalytic surfaces depend critically on the detailed structure of the surface, which can be controlled by adding agents that may themselves take no direct part in the chemical reactions.[141]

The above lines are applicable to micelle-catalyzed reactions. A solution containing micellar aggregates is macroscopically homogeneous

(i.e., is one phase). However, microscopically this phase is separated into many small regions of high solute concentration (micelles) dispersed in a solvent region. Any reactive species added to the solution distributes itself between these regions. If the conditions in these two environments result in different reaction rates, then the micelles act as either catalysts or inhibitors.[142] The catalytic efficiency is governed both by the affinity of the reagents for the micelles and by the reactivity of the bound reagent molecules.

Surfactant micelles provide a unique microenvironment for the compounds when they are solubilized in an aqueous solution. Surfactant micelles are able to provide either a polar region or a region of high charge density, accompanied by an electrostatic potential of up to a few hundred millivolts at the micellar surface, and a nonpolar hydrophobic region in the micellar core. Micelle aggregation numbers usually range from less than 100 for ionic surfactants to several hundred for nonionic surfactants. Therefore, the kinetics of micellar solutions is governed by electrostatic and hydrophobic interactions between micelles and reactants, transition complexes, and products. It is logical, therefore, that a combination of hydrophobic and electrostatic interactions result in the orientation and concentration of polar or charged compounds in ways that are not possible in

simple solutions in organic solvents. If any of the reaction species interacts with micelles, then the presence of micelles affect the reaction rate.

The observed rate of a chemical reaction (R_ψ) in micellar solutions is considered to be the sum of the rates in the continuous aqueous phase (R_w) and micellar pseudophase (R_m).[22,23]

$$R_\psi = R_w + R_m \qquad (1.4)$$

Thus, for a bimolecular reaction between A and B in aqueous micelles:

$$k_\psi [A] [B] = k_w [A]_w [B]_w + k_m [A]_m [B]_m \qquad (1.5)$$

where observed rate constant k_ψ is found on the basis of the moles of A and B in the total volume of the system, V_t . Subscript w refers to the water phase and subscript m to the micellar phase. In the simplest case, both reactants are entirely bound to the micelles and the reaction takes place completely in the micellar phase. The rate of reaction in water can be neglegted, so that the first term on the right hand side of Eq. 1.5 is negligible. This leads to the expression:

$$k_\psi = k_m [A]_m [B]_m / [A] [B] \qquad (1.6)$$

For this special case of totally bound reactants $[A]_m = [A] / \phi_m$ and $[B]_m = [B] / \phi_m$, where ϕ_m is the volume fraction of the micellar phase. Using these realations in Eq. 1.6 gives:

$$k_\psi = k_m / \phi^2_m \qquad (1.7)$$

Eq. 1.7 shows that the observed rate is enhanced by compartmentalization of reactants into the reaction volume $V_t\ \phi_m$, producing an apparent catalysis. Rate enhancement is mainly a consequence of high reactant concentrations in the micellar volume, which contains all the reactants. Eqs. 1.5 and 1.6 can also explain kinetic control of selectivity of catalytic reactions in micelles. If the two reactants are spatially separated in micellar and water phases by virtue of their solubility properties, the rate of reaction is decreased compared to the case where both reactants are present only in the micellar phase.

Ninhydrin –α-isoleucine reaction has been used as prototype to investigate the catalytic activity of gemini surfactants.

Importance of the Research Problem

"Gemini surfactants" have structures and properties, which are different from those of monomeric surfactants and are said to be "unique to the world of surfactants". These surfactants show high surface activity, unusual viscosity changes with an increase in [surfactant], a low critical micelle concentration (cmc), and unusual micellar structures. Geminis have already been utilized in many fields as in skin care, antibacterial regimens, construction of high porosity materials, analytical separation and solubilization process.[13-17]

Survey of available literature reveals that no serious attempt has been made to study the micellization phenomenon of gemini surfactants in polar non-aqueous solvents. The micellization tendency of the surfactants decrease in presence of organic solvents. Detailed study showed that the gemini nearly outclass the micellization arresting property of solvents. The implications of the results obtained of gemini micellization in polar-nonaqueous solvents may be useful in micellar catalysis.

A vast majority of experimental data are available on solution/aggregational behavior of conventional surfactants in presence of different classes of additives. Most studies on geminis also are related to their specific aggregation behavior and structural properties[143-145] but morphological studies of geminis in the presence of different class of additives has not been systematically investigated. Being an entirely a new field of research, additive effects were studied by viscometriy and DLS techniques. From a practical point of view, the presence of non-spherical micelles gives solution a very high viscosity which might be of importance in industrial formulations as it may enhance performance and customer appeal of formulation.

The use of ninhydrin for the detection and estimation of amino acids has been the subject of various investigations because of its potential ability

to reveal latent fingerprints.[146] The use depends on the formation of a purple-colored product (*Ruhemann's purple*) whose amount depends upon reaction conditions, i.e., pH, temperature, reactant concentrations, etc.[147] The technique, although useful, still has room for improvements. With the view that the method could find applications to improve contrast and visualization of ninhydrin-developed fingerprints and may prove a step forward from the methods already used in current forensic research, systematic kinetic studies were performed of the ninhydrin-L-isoleucine reaction in the presence of micellar media. Due to improved performance of geminis on almost all fronts for which conventional surfactants are utilized, effects of three synthesized geminis on the rate of ninhydrin-L-isoleucine reaction were studied in detail. Optimum conditions can be obtained by studying the effect of various factors on the rate and extent of the reaction. The reaction rates are enhanced as compared to conventional surfactants.

The Lay – Out of the Thesis

Chapter–I. General Introduction.

Chapter–II. Experimental

Chapter–III. Micellization phenomenon of gemini surfactants in polar nonaqueous-water mixed solvents.

Chapter–IV. Viscometric and DLS studies on aqueous gemini surfactants in presence of additives.

Chapter–V. Catalytic activity of gemini surfactants and effect of organic solvents on the ninhydrin-L-isoleucine reaction.

References

1. F. M. Menger and C.A. Littau, *J. Am. Chem. Soc.*, **113**, 1451 (1991).
2. F. M. Menger and C.A. Littau, *J. Am. Chem. Soc.*, **115**, 10083 (1993).
3. R. Zana, M. Benrraou and R. Rueff, *Langmuir*, **7**, 1072 (1991).
4. C. A. Bunton, L. Robinson, J. Schaak and M. F. Stern, *J. Org. Chem.*, **36**, 2346 (1971).
5. F. Devinsky, I. Lacko, D. Mlynarcik, V. Racansky and L. Krasnec, *Tensides Detergents,* **22**, 1 (1985).
6. Y. –P. Zhu, A. Masuyama and M. Okahara, *J. Am. Oil Chem. Soc.*, **67**, 459 (1990).
7. M. J. L. Castro, J. Kovensky and A. F. Cirelli, *Tetrahedron Lett.*, **38**, 3995 (1997).
8. P. Renouf, C. Mioskowski, L. Lebeau, D. Hebrault and J. R. Desmurs, *Tetrahedron Lett.*, **39**, 1357 (1998).
9. R. Oda, I. Huc and S. J. Candau, *Chem. Commun.*, 2105 (1997).
10. R. Zana, H. Levy, D. Papoutsi and G. Beinert, *Langmuir* **11**, 3694 (1995).

11. M. J. Rosen, T. Gao, Y. Nakatsuji and A. Masuyama, *Colloids Surf. A*, **88**, 1 (1994).

12. K. Esumi, M. Goino and Y. Koide, *J.Colloid Interface Sci.*, **183**, 539 (1996).

13. P. V. D. Voort, M. Mathieu, F. Mees and E. F. Vansant, *J. Phys. Chem. B*, **102**, 8847 (1998).

14. K. Chen, D. C. Locke, T. Maldacker, J. L. Lin, S. Aawasiripong and U. Schurrath, *J. Chromatogr. A*, **822**, 281 (1998).

15. M. Dreja and B. Tieke, *Langmuir*, **14**, 800 (1998).

16. F. Li and M. J. Rosen, *J. Colloid Interface Sci.*, **224**, 265 (2000).

17. M. Pavilikova, I. Lacko, F. Devinsky and D. Nlynarak, *Follect. Czech. Chem. Commun.*, **60**, 1213 (1995).

18. R. Zana and Y. Talmon, *Nature* **362**, 228 (1993).

19. W. C. Preston, *J. Phys. Chem.*, **52**, 84 (1948).

20. P. Mukerjee and K. J. Mysels, *Natl. Stand. Ref. Data Ser.* (U. S. Natl. Bur. Stand) No. 36 (1971).

21. G. C. Kresheck, in "*Water: A Comprehensive Treatise*", Edited by F. Franks, Plenum Press, New York, Vol. 4., p. 96 (1975).

22. J. H. Fendler and E. Fendler, "*Catalysis in Micellar and Macromolecular Systems*", Academic Press, New York (1975).

23. J. H. Fendler, "*Membrane Mimetic Chemistry*", Wiley, New York (1982).

24. D. G. Davis and C. R. Bury, *J. Chem. Soc.*, 2263 (1930).

25. M. Gratzel, "*Heterogeneous Photochemical Electron Transfer*", CRS Press, Boca Raton, FL (1989).

26. M. J. Schick, *J. Colloid Interface Sci.*, **17**, 801 (1962).

27. A. Ray and G. Nemethy, *J. Am. Chem. Soc.*, **93**, 6787 (1971).

28. R. F. Tuddenham and A. E. Alexander, *J. Phys. Chem.*, **66**, 1839 (1962).

29. M. Yamanaka, M. Aratono, K. Motomura and R. Matura, *Colloid Polym. Sci.*, **262**, 338 (1984).

30. Y. Ikawa, S. Tsuru, Y. Murata, M. Okawauchi, M. Shigematsu and G. Sugihara, *J. Solution Chem.*, **17**, 125 (1988).

31. N. Nishikido, N. Yoshinura, M. Tanaka and S. Kaneshina, *J. Colloid Interface Sci.*, **78**, 338 (1980).

32. S. D. Hanmann, *J. Phys. Chem.*, **66**, 1359 (1962).

33. N. Nishikido, N. Yoshimura and M. Tanaka, *J. Phys. Chem.*, **84**, 559 (1980).

34. P. T. T. Wong and H. H. Mantsch, *J. Colloid Interface Sci.*, **129**, 258 (1989).

35. M. Tanaka, S. Kaneshina, S. Kuramoto and R. Matuura, *Bull. Chem. Soc. Jpn.*, **48**, 432 (1975).

36. S. Rodriguez and H. Offen, *J. Phys. Chem.*, **81**, 47 (1977).

37. A. Ray, *J. Am. Chem. Soc.*, **91**, 6511 (1969).

38. A. Chatterjee, S. Maiti, S.K. Sanyal and S. P. Moulik, *Langmuir*, **18**, 2998 (2002).

39. J. –H. Kim, M. M. Domach and R. D. Tilton, *Langmuir*, **16**, 10037 (2000).

40. C. Tanford, " *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*", Wiley, New York (1980).

41. M. J. Rosen, "*Surfactants and Interfacial Phenomenon*", John Wiley, New York (1989).

42. S. Kumar, A. Z. Naqvi, V. K. Aswal, P. S. Goyal and Kabir-ud-Din, *Curr. Sci.*, **84**, 1346 (2003).

43. E. Junquera and E. Aicart, *Langmuir*, **18**, 9250 (2002).

44. R. Rangnathan, M. Peric, R. Medina, U. Garcia and B. L. Bales, *Langmuir*, **17**, 6765 (2001).

45. N. Gorski and J. Kalus, *Langmuir*, **17**, 4211 (2001).

46. M. Benrraou, B. L. Bales and R. Zana, *J. Phys. Chem. B*, **107**, 13432 (2003).

47. N. Jain, V. K. Aswal, P. S. Goyal, P. Bahadur, *J. Phys. Chem. B*, **102**, 8452 (1998).

48. H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem. Int. Ed. Engl.*, 27, 113 (1988).

49. H. – H. Kohler and L. Sepulveda, *J. Colloid Interface Sci.*, **113**, 566 (1986).

50. Y. Hendrikx, J. Charvolin and M. Rawiso, *J. Colloid Interface Sci.*, **113**, 566 (1986).

51. G. W. Gray and P. A. Windsor, in " *Advances in Chemistry Series*": Edited by R. F. Gould, ACS, Washington, DC (1967).

52. T. Kotoka, *Langmuir*, **5**, 398 (1989).

53. S. S. Berr and R. R. Jones, *Langmuir*, **4**, 1247 (1988).

54. H. Hoffmann, H. S. Kielman, D. Pavlovic, G. Platz and W. Ulbricht, *J. Colloid Interface Sci.*, **80**, 237 (1981).

55. J. Mata, D. Varade, G. Ghosh and P. Bahadur, *Colloids Surf. A*, **245**, 69 (2004).

56. J. Mata, T. Joshi, D. Varade, G. Ghosh and P. Bahadur, *Colloids Surf. A*, **247**, 1 (2004).

57. J. Lang, A. Djavanbakht and R. Zana, *J. Phys. Chem.*, **84**, 1541 (1980).

58. M. Almgren and S. Swarup, *J. Phys. Chem.*, **87**, 876 (1983).

59. P. Lianos and R. Zana, *J. Phys. Chem.*, **84**, 3339 (1980).

60. P. J. Missel, N. A. Mazer, G. B. Benedek, C. Y. Young and M. C. Carey, *J. Phys. Chem.*, **84**, 1044 (1980).

61. S. Ikeda, S. Hayashi and T. Imae, *J. Phys. Chem.*, **85**, 106 (1981).

62. G. Porte and J. Appell, *J. Phys. Chem.*, **85**, 2511 (1981).

63. S. Ozeki and S. Ikeda, *J. Colloid Interface Sci.*, **87**, 424 (1982).

64. S. Ozeki and S. Ikeda, *J. Colloid Interface Sci.*, **77**, 219 (1980).

65. H. Hoffmann, G. Platz, H. Rehage, W. Schorr, *Ber. Bunsen.* Ges. *J. Phys. Chem.*, **85**, 877 (1981).

66. H. Hoffmann, G. Platz, H. Rehage and W. Schorr, *Adv. Colloid Interface Sci.*, **11**, 275 (1982).

67. C. Gamboa and L. Sepulveda, *J. Colloid Interface Sci.*, **113**, 566 (1986).

68. V. K. Aswal, P. S. Goyal and P. Thiyagarajan, *J. Phys. Chem. B*, **102**, 2469 (1998).

69. H. A. Scheraga and J. K. Backus, *J. Am. Chem. Soc.*, **73**, 5108 (1951).

70. P. G. Cummins, E. Staples, J. B. Hayter and J. Penfold, *J. Chem. Soc., Faraday Trans. I*, **83**, 2773 (1987).

71. J. Marignan, J. Appell, P. Bassereau, G. Porte and R. P. May, *J. Physique* (Paris), **50**, 3553 (1989).

72. J. Penfold, E. Staples and P. G. Cummins, *Adv. Colloid Interface Sci.*, **34**, 451 (1991).

73. T. Clausen, P. K. Vinson, J. R. Minter, H. T. Davis, Y. Talmon and W. G. Miller, *J. Phys. Chem.*, **96**, 474 (1992).

74. Z. Lin, L. E. Scriven and H. T. Davis, *Langmuir*, **8**, 2200 (1992).

75. D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. II*, **77**, 601 (1981).

76. H. Hoffmann, *Adv. Colloid Interface Sci.*, **32**, 123 (1990).

77. J. N. Israelachvili, "*Intermolecular and Surface Forces*", 2nd ed., Academic, London (1991).

78. J. N. Israelaachvili, S. Marcelja and R. G. Horn, *Rev. Biophys.*, **13**, 121 (1980).

79. C. Tanford, *J. Phys. Chem.*, **76**, 3020 (1972).

80. J. N. Phillips, *Trans. Faraday Soc.*, **51**, 561 (1955).

81. H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

82. E. R. Nightingale, *J. Phys. Chem.*, **66**, 894 (1962).

83. M. V. Oko and R. L. Venable, *J. Colloid Interface Sci.*, **35**, 53 (1971).

84. C. Tondre and R. Zana, *J. Phys. Chem.*, **76**, 3451 (1972).

85. H. Wennerstrom and B. Lindman, *Phys. Rep.*, **52**, 1 (1979).

86. D. Bartet, C. Gamboa and L. Sepulveda, *J. Phys. Chem.*, **84**, 272 (1980).

87. C. Gamboa, L. Sepulveda and R. Soto, *J. Phys. Chem.*, **85**, 1429 (1981).

88. R. Nagarajan, K. Shah and S. Hammond, *Colloids Surf. A*, **4**, 147 (1982).

89. D. Shoemaker, C. Garland, J. Steinfeld and N. Nibler, in "*Experiments in Physical Chemistry*": 4th ed., Mc Grew-Hill, New York (1984).

90. L. Sepulveda and J. Cortes, *J. Phys. Chem.*, **89**, 5322 (1985).

91. M. Meyer, W. Cabrera, C. Gamboa and L. Sepulveda, *J. Colloid Interface Sci.*, **117**, 460 (1987).

92. C. A. Bunton and C. P. Cowell, *J. Colloid Interface Sci.*, **122**, 154 (1988).

93. R. B. Dorshaw, J. Briggs, C. A. Bunton and D. F. Nicoli, *J. Phys. Chem.*, **86**, 2388 (1982).

94. R. B. Dorshaw, C. A. Bunton and D. F. Nicoli, *J. Phys. Chem.*, **87**, 1409 (1983).

95. S. J. Candau, E. Hirsch and R. Zana, *J. Colloid Interface Sci.*, **105**, 521 (1985).

96. T. Imae, A. Abe, Y. Taguchi and S. Ikeda, *J. Colloid Interface Sci.*, **109**, 567 (1986).

97. T. Imae and S. Ikeda, *J. Phys. Chem.*, **90**, 5216 (1986).

98. F. A. L. Anet, *J. Am. Chem. Soc.*, **108**, 7102 (1986).

99. J. Kalus and H. Hoffmann, *J. Phys. Chem.*, **87**, 714 (1987).

100. A. Abe, T. Imae and S. Ikeda, *Colloid Polym. Sci.*, **265**, 637 (1987).

101. H. Hoffmann, U. Kraemer and H. Thurn, *J. Phys. Chem.*, **94**, 2027 (1990).

102. J. Appell, G. Porte, A. Khatory, F. Kern and S. J. Candau, *J. Phys. II*, **2**, 1045 (1992).

103. X. L. Wu, C. Yeung, M. W. Kim, J. S. Huang and D. Ou-Yang, *Phys. Rev. Lett.*, **68**, 1426 (1992).

104. D. Danino, Y. Talmon, H. Levy, G. Beinert and R. Zana, *Science*, **269**, 1420 (1995).

105. P. D. Butler, L. J. Magid, N. A. Hamilton, J. B. Hayter, B. Hammouda and P. J. Kreka, *J. Phys. Chem.*, **100**, 442 (1996).

106. "*Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*", Edited by V. Degiorgio and M. Corti, Elsevier, Amsterdam (1985).

107. B. Lindman and H. Wennerstrom, *Top. Current Chem.*, **87**, 32 (1980).

108. P. Mukerjee, K. J. Mysels and P. Kapauan, *J. Phys. Chem.*, **71**, 4166 (1967).

109. L. S. Romsted, in " *Surfactants in Solution*", Edited by K. L. Mittal and B. Lindman, Plenum Press, New York, Vol. 2 (1984).

110. L. S. Romsted, in "*Micellization, Solubilization and Microemulsions*", Edited by K. L. Mittal, Plenum, New York, Vol. 2, p. 589 (1977).

111. L. S. Romsted, Ph. D. Thesis, Indiana university (1975).

112. C. Gamboa, L. Sepulveda and R. Soto, *J. Phys. Chem.*, **85**, 1429 (1981).

113. B. W. Ninham and D. F. Evans, *Faraday Discuss Chem. Soc.*, **81** (1986).

114. D. D. Lasic, *J. Colloid Inerface Sci.*, **124**, 428 (1988).

115. H. Hauser, *Biochim. Biophys. Acta*, **772**, 37 (1984).

116. E. W. Kaler, K. L. Herrinton, A. K. Murthy and J. A. N. Zasadzinski, *J. Phys. Chem.*, **96**, 6698 (1992).

117. (a) R. Strey, W. John, G. Porte and P. Bassereau, *Langmuir*, **6**, 1635 (1990). (b) H. Hoffmann, C. Thunig, U. Munkert, H. W. Meyer and W. Richter, *Langmuir*, **8**, 2629 (1992).

118. P. Herve, D. roux, A. M. Belocq, F. Nallet and T. Gulik-Krzywicki, *J. Phys. II*, **3**, 1255 (1993).

119. A. Jurgens, *Tenside Surf. Deterg.*, **26**, 222 (1989).

120. J. C. vande Pas, *Tenside Surf. Deterg.*, **28**, 158 (1991).

121. J. C. Vande Pas and C. Buytenhek, *J. Colloids Surf.*, **68**, 127 (1992).

122. A. Sein, J. B. F. N. Engberts, E. Linden, J. C. van de Pas, *Langmuir*, **9**, 1714 (1993).

123. P. Stilbs, *J. Colloid Interface Sci.*, **87**, 385 (1982).

124. P. Stilbs, *J. Colloid Interface Sci.*, **89**, 547 (1982).

125. S. Gupta and S. Sharma, *J. Indian Chem. Soc.*, **42**, 855 (1965).

126. T. Yamashita, H. Yano, S. Harada and T. Yasunaga, *J. Phys. Chem.*, **87**, 5482 (1983).

127. K. R. Wormuth and E. W. Kaler, *J. Phys. Chem.*, **91**, 611 (1987).

128. P. M. Lindemuth and G. L. Bertrand, *J. Phys. Chem.*, **97**, 7769 (1993).

129. Kabir-ud-Din, S. Kumar, V. K. Aswal, P. S. Goyal, *J. Chem. Soc., Faraday Trans.*, **92**, 2413 (1996).

130. Ch. D. Prasad and H. N Singh, *Colloids Surfs.*, **59**, 27 (1991).

131. S. Kumar, D. Bansal and Kabir-ud-Din, *Langmuir*, **15**, 4960 (1999).

132. S. Kumar, D. Sharma and Kabir-ud-Din, *J. Surf. Deterg.*, **6**, 339 (2003).

133. S. Kumar, D. Sharma and Kabir-ud-Din, *J. Surf. Deterg.*, **7**, 75 (2004).

134. Kabir-ud-Din, S. Kumar, Kirti and P. S. Goyal, *Langmuir*, **12**, 1490 (1996).

135. Kabir-ud-Din, D. Bansal and S. Kumar, *Langmuir*, **13**, 5071 (1997).

136. S. Kumar, A. Z. Naqvi and Kabir-ud-Din, *Langmuir*, **16**, 5252 (2000).

137. S. Kumar, A. Z. Naqvi and Kabir-ud-Din, *Langmuir*, **17**, 4787 (2001).

138. Ch. D. Prasad and H. N Singh, *Colloids Surfs.*, **50**, 37 (1990)

139. V. Rajagopalan, P. S. Goyal, B. S. Valaulikar and B. A. Dasannacharya, *Physica B*, **180 & 181**, 525 (1992).

140. S. Kumar, Kirti and Kabir-ud-Din, *J. Am. Oil. Chem. Soc.*, **71**, 763 (1994).

141. C. A. Bunton, *Prog. Solid State Chem.*, **8**, 239 (1973).

142. H. Morawetz, *Adv. Catal.*, **20**, 341 (1969).

143. F. Devinsky, I. Lacko, T. Imam, *J. Colloid Inerface Sci.*, **143**, 336 (1993).

144. Th. Dam, J. B. F. N. Engberts, J. Karthauser, S. Karaborni, N. M. Van Os, *Colloids Surfs. A.*, **118**, 41 (1996).

145. E. Buhler, E. Mendes, P. Boltenhagen, J. P. Munch, R. Zana, S. J. Candau, *Langmuir,* **13**, 3096 (1997).

146. (a). M. M. Joullie, T. R. Thompson and N. H. Nemeroff, *Tetrahedron*, **47**, 8791 (1991). (b). S. Oden and B. Von Hofsten, *Nature*, **173**, 449 (1954). (c). J. Almog, in "*Advances in Fingerprint Technology*", Edited by H. Lee and R. E. Gaensslen, Elseveir Science, New York (1991).

147. (a). Z. Khan and A. A. Khan, *J. Indian Chem. Soc.*, **66**, 454 (1989). (b). Z. Khan and A. A. Khan, *J. Indian Chem. Soc.*, **67**, 963 (1990). (c). Z. Khan, D. Gupta and A. A. Khan, *Int. J. Chem. Kinet.*, **24**, 481 (19).

Chapter-II

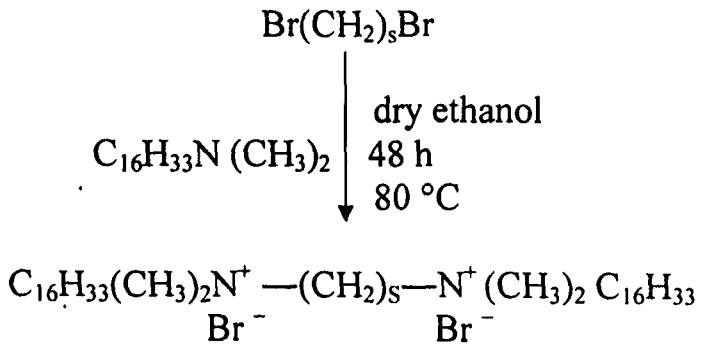
Experimental

Materials

The materials used throughout the study are given in Table 2.1, which also includes their abbreviation, chemical formula, make and purity.

Synthesis of Gemini Surfactants:

There are two main factors which are important in their preparation: one is synthesis and the other is purification. Simple cationic geminis of hexadecyl series with methyl spacers were prepared as shown in Scheme 2.1. This method is attractive when the dibromide is reactive and commercially available and is preferable only for $s \geq 3$.[1] Typically, a mixture of *N*, *N*- dimethylhexadecylamine and α, ω – dibromoalkane (molar ratio 2.1:1) was boiled under reflux in dry ethanol and stirring was continued at 80 °C for 48h to ensure as much as possible a complete biquaternization. The progress of the reaction was monitored by using TLC technique.



(s = 4, 5, 6)

Scheme 2.1

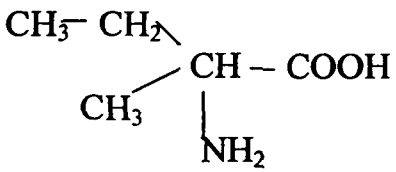
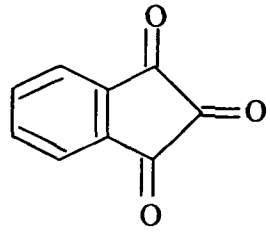
Table 2.1: Names and structural formulas of the chemicals used.

Name	Abbreviation	Structural Formula	Make	% Purity
1. <u>Surfactants</u>				
cetyltrimethylammonium bromide	CTAB	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$	BDH (England)	≥ 99.0
bis(hexadecyldimethylammonium) butane dibromide	16-4-16	n-$C_{16}H_{33}(CH_3)_2N^+$-$(CH_2)_4$-N^+-$(CH_3)_2C_{16}H_{33}$-n, 2 Br^-	synthesized	-
bis(hexadecyldimethylammonium) pentane dibromide	16-5-16	n-$C_{16}H_{33}(CH_3)_2N^+$-$(CH_2)_5$-N^+-$(CH_3)_2C_{16}H_{33}$-n, 2 Br^-	synthesized	-
bis(hexadecyldimethylammonium) hexane dibromide	16-6-16	n-$C_{16}H_{33}(CH_3)_2N^+$-$(CH_2)_6$-N^+-$(CH_3)_2C_{16}H_{33}$-n, 2 Br^-	synthesized	-
2 (a). <u>Reagents for synthesis</u>				
1,4- dibromobutane	-	Br-$(CH_2)_4$-Br	Fluka (Switzerland)	≥ 98.0
1,5- dibromopentane	-	Br-$(CH_2)_5$-Br	Fluka (Switzerland)	≥ 98.0

Contd...

1,6- dibromohexane	-	$Br-(CH_2)_6-Br$	Fluka (Switzerland)	≥ 97.0
***N,N*-dimethylhexadecylamine**	-	$(CH_3)_2N-(CH_2)_{15}-CH_3$	Fluka (Switzerland)	≥ 99.0

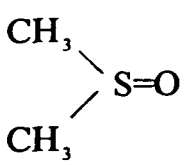
2 (b). <u>Reagents for kinetics</u>

L-isoleucine	Ile		s.d.fine (India)	99.0
ninhydrin	nin		E.Merck (India)	99.0

3. <u>Others</u>

acetonitrile	AN	CH_3CN	E.Merck (India)	99.5
methyl cellosolve	MC	$HO-CH_2-CH_2-O-CH_3$	s.d.fine (India)	99.0

Contd...

dimethyl sulfoxide	DMSO		E.Merck (India)	99.0
hexane	-	CH_3-$(CH_3)_4$-CH_3	s.d.fine (India)	99.0
ethylacetate	EtOAc	$CH_3COOC_2H_5$	s.d.fine (India)	99.7
ethanol absolute	EtOH	CH_3CH_2OH	Merck (Germany)	99.8
1- propanol	PrOH	$CH_3CH_2CH_2OH$	E.Merck (India)	99.0
n-butanol	C_4OH	$CH_3(CH_2)_3OH$	BDH (England)	≥99.0
n-pentanol	C_5OH	$CH_3(CH_2)_4OH$	BDH (England)	≥99.0
n-hexanol	C_6OH	$CH_3(CH_2)_5OH$	BDH (England)	≥99.0
n-hexylamine	C_6NH_2	$CH_3(CH_2)_5NH_2$	Fluka (Switzerland)	≥99.0
potassium bromide	-	KBr	E.Merck (India)	99.0
sodium acetate	-	CH_3COONa	E.Merck (India)	99.0
acetic acid	-	CH_3COOH	E.Merck (India)	99.0

The solvent was removed under vacuum after the completion of the reaction and the residue was obtained with a 70-90% yield by successive recrystallization (at least three times) by hexane/ethylacetate mixture.

The purity of the gemini is critical as the surface activity can be changed in the presence of traces of impurities. Therefore, after recrystallizations, all the three surfactants were characterized by ^{1}H NMR, FT-IR, mass spectroscopy and elemental analysis. All the values obtained were satisfying, which indicated that the surfactants were well purified. Spectral and elemental analysis data for the geminis are collected in Table 2.2.

The purity of the gemini surfactants was further ensured by the absence of minimum in surface tension vs. log [gemini] plots.[2]

Preparation of Solutions

Dimineralized double-distilled water (over alkaline $KMnO_4$ in an all-Pyrex glass distillation set-up) was used throughout (specific conductivity: (1-2) x 10^{-6} S cm^{-1}), except for the DLS experiments where second-stage milli Q water with a specific conductivity of 0.053 x 10^{-6} S cm^{-1} was used.

Table 2.2: Analytical characteristics of the geminis.

Compound	Elemental analysis % found (calc.)	^{1}H NMR δ (ppm) (solvent $CDCl_3$)	MS-ESI m/z (%)	IR ν_{max} (KBr) C–N (cm^{-1})
16-4-16	C 63.49 (63.62)	0.88 (t, 6H, alkyl chain 2 x 1 CH_3)	676 (M^+–Br, 19.63)	1043.08
	H 11.65 (11.40)	1.257-1.344 (br m, 44H, alkyl chain 2 x 11 CH_2)	404 (100.0)	
	N 3.40 (3.71)	1.754 (m, 12 H, alkyl chain 2 x 3 CH_2)	324 (62.27)	
		2.084 (br s, 4H, spacer chain 1 x 2 $CH_2CH_2N^+$)	310 (44.78)	
		3.308 (s, 12H, 2 x 2 N^+CH_3)	297 (6.75)	
		3.431 (m, 4H, alkyl chain 2 x 1 CH_2N^+)	268 (7.97)	
		3.811 (br s, 4H, spacer chain 2 x 1 CH_2N^+)	197 (12.88)	
			155 (13.50)	
16-5-16	C 64.28 (64.06)	0.88 (t, 6H, alkyl chain 2 x 1 CH_3)	689 (M^+–Br, 63.19)	1230.3-1044.5
	H 11.99 (11.45)	1.255-1.352 (br m, 42H, alkyl chain 2 x 10 CH_2, spacer chain $1CH_2$)	418 (11.96)	
	N 3.43 (3.64)	1.610-1.725 (crude t, 16H, alkyl chain 2 x 4 CH_2)	384 (20.55)	

Contd...

		1.987-2.116 (br m, 4H, spacer chain 1 x 2 $CH_2CH_2N^+$)	304 (100.0)	
		3.352 (s, 12H, 2 x 2 N^+CH_3)	270 (9.50)	
		3.45-3.505 (crude t, 4H, alkyl chain 2 x 1 CH_2N^+)	192 (12.27)	
		3.844-3.90 (crude t, 4H, spacer chain 1 x 2 CH_2N^+)	114 (77.91)	
16-6-16	C 64.71 (64.43)	0.88 (t, 6H, alkyl chain 2 x 1 CH_3)	701 (M^+–Br, 78.52)	1242.7
	H 11.81 (11.58)	1.255-1.350 (s + br m, 48H, alkyl chain 2 x 12 CH_2)	607 (7.97)	
	N 3.66 (3.58)	1.580-1.715 (br m, 12H, spacer chain 1 x 2 $CH_2CH_2N^+$, alkyl chain 2 x 1 $CH_2CH_2CH_2N^+$)	432 (9.82)	
		1.995 (br s, 4H, spacer chain 1 x 2 $CH_2CH_2CH_2N^+$)	398 (28.22)	
		3.355 (br s, 16H, 2 x 2 N^+CH_3, alkyl chain 2 x 1 CH_2N^+)	311 (100.0)	
		3.431-3.686 (m, 4H, spacer chain 1 x 2 CH_2N^+)	270 (27.92)	
			199 (16.56)	
			128 (34.35)	

Buffer Solutions: For kinetic study, all the surfactants, ninhydrin and amino acid solutions were prepared in sodium acetate-acetic acid buffer of required pH. The ninhydrin stock solution was stored in a dark bottle.

The buffers were prepared by mixing appropriate volumes of 0.20 mol dm^{-3} acetic acid and 0.20 mol dm^{-3} sodium acetate solutions.[3]

Instrumentation

Surface Tension Measurements: A du Nouy type tensiometer (Hardson and Co., Kolkata) was used. Surface tension measurements of surfactants at the air-water interface are the most often applied method for determining cmc. Since pure water at room temperature has a surface tension of about 72 mN/m and the surface tension of the air-water interface when coated with a monolayer of amphiphile is generally in the 20-40 mN/m range, one can observe a break in surface tension as a function of surfactant concentration.

Conductance Measurements: The critical micelle concentrations (cmc' s) and degree of counter-ion dissociation (α values) were determined by this method. The measurements were performed on an ELICO (type CM 82T) bridge equipped with platinized electrodes (cell constant = 1.02 cm^{-1}). The conductivity runs were carried out by adding progressively concentrated surfactant stock solution into the thermostated solvent. The cmc values were

obtained from the break point of nearly two straight lines of the specific conductance vs. concentration plots.[4]

Viscometric Measurements: In the present study the viscosity measurements were carried out using an Ubbelohde suspended level capillary viscometer thermostated at 30 ± 0.1 °C. The viscometer was cleaned and dried before each measurement. The flow time for constant volume of solution through the capillary was measured with a calibrated stopwatch.

pH – Measurements: pH measurements of the solutions were made with an ELICO pH-meter type LI-120 (ELICO, Hyderabad, India) fitted with an ELICO CH-41 glass and calomel combination electrode. The electrode was stored in pH 7 buffer and was washed in de-ionized double-distilled water before use. It was then rinsed with pH 7 buffer and the pH-meter was standardized using pH 4 buffer solution. Whenever the solution was changed, the electrode was rinsed with double-distilled water and the surplus water was removed and the pH-meter was restandardized using the pH 4 buffer solution. All pH measurements were made at least in triplicate and they agreed within ± 0.02.

Dynamic Light Scattering Measurements: A home-built set up was used for the DLS experiments[5,6] (Fig. 2.1). The incident beam was generated from a vertically polarized 15 mW He-Ne laser source (λ = 6328 Å) fixed at one arm of a goniometer. The scattered beam was passed through a vertical

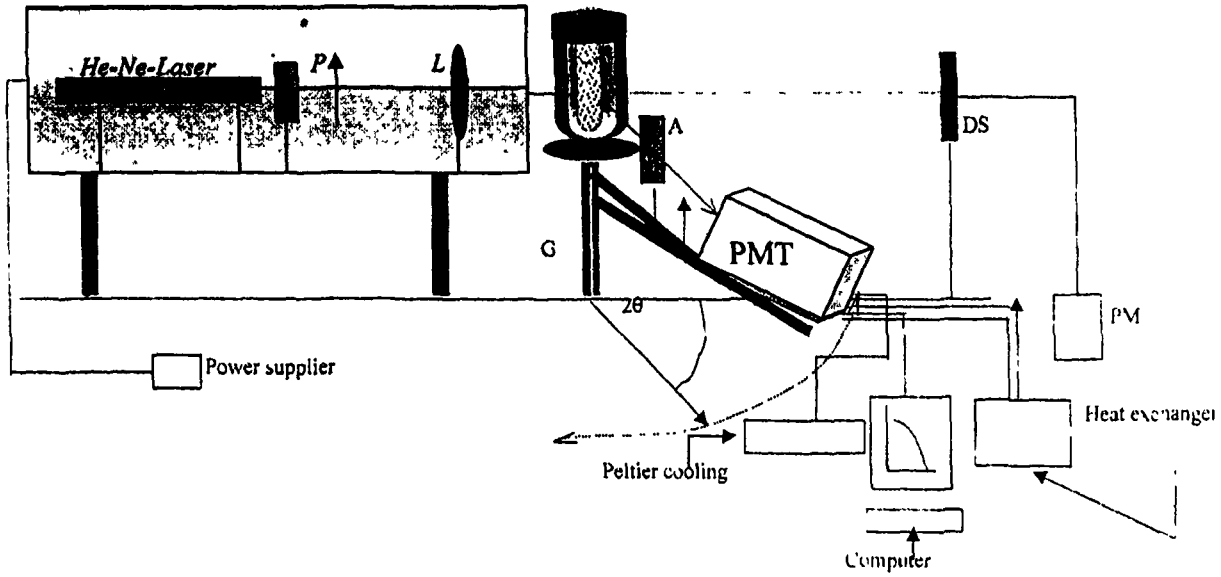


Fig. 2.1: Schematic diagram of a DLS diffractometer.

P and A: Glan-Thomson polarizers, L: A plano-convex lens (f = 150 mm), PMT: Photo-multiplier tube detector, G: Goniometer, DS: Diode sensor, PM: Power meter

polarizer (Glan-Thomson polarizer) and counted by a photo-multiplier tube (PMT) at 90°, mounted on the other arm of the goniometer. Before measurement, each sample was centrifuged at 15,000 rpm for 30 min to remove 'dust' particles. The sample was then loaded onto an optical-quality 10 nm diameter quartz cell. The sample cell was placed inside a borosilicate cuvette consisting of an index matching liquid (e.g., decalene) and aligned

with the axis-of-rotation of the goniometer. Scattered photons from dispersed aggregates were counted by the PMT detector, which was operated at 5 °C. The output current from the PMT was then suitably amplified and digitized through various electronics before it was fed to a channel digital correlator (Malven, U.K., model auto-sizer 4700). The whole assembly was placed on a vibration – free table. All correlation spectra were recorded at 30±0.1 °C. Because the count rate was observed to be on the low side, data collection time was increased for each solution to improve the statistics of the DLS. The errors in the measurements of micellar sizes from DLS spectra are within ±3% around the mean value of three best measurements of each sample.

Kinetic Measurements: The kinetic measurements were made spectrophotometrically by measuring the absorbance by Bausch & Lomb Spectronic-20 spectrophotometer. The progress of the reaction was followed by measuring the absorbance of purple color (reaction product) at different intervals of time at 570 nm.[7]

Thermostat: A thermostatic water bath, designed and assembled in the laboratory with commercially available components, was used. The temperature was controlled within ±0.1 °C.

^{1}H NMR Measurements: ^{1}H NMR spectra for the characterization of the synthesized geminis were recorded on a 300 MHz Bruker Cryomagnet spectrometer in $CDCl_3$ with ^{1}H chemical shifts relative to internal TMS.

Elemental Analysis: Microanalysis were performed on elemental analyzer and are recorded as percentages.

Mass Spectroscopy: The electrospray mass spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. The samples (dissolved in suitable solvents such as methanol/acetonitrile/water) were introduced into the ESI source through a syringe pump at the rate of 5 µl per min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. The spectra were collected in 6s scans and the print outs are averaged spectra of 6-8 scans.

FT-IR Measurements: The IR spectra were recorded using a FT-IR Spectrometer Interspec 2020 (Spectrolab, U. K.) with KBr used as a medium.

References

1. R. Zana, M. Benrraou and R. Rueff, *Langmuir*, **7**, 1072 (1991).

2. K. S. Sharma, C. Rodgers, R. M. Palepu and A. K. Rakshit, *J. Colloid Interface Sci.*, **268,** 482 (2003).

3. H. T. S. Britton, " *Hydrogen Ions*", Chapman and Hall, London, Vol. 1 (1942).

4. P. Mukerjee and K. J. Mysels, "*Critical Micelle Concentrations of Aqueous Surfactant Systems*" : NSRDS – NBS 36, Superintendent of Documents, Washington, D. C. (1971).

5. J. Mata, D. Varade, G. Ghosh and P. Bahadur, *Colloids Surf. A.*, **245,** 69 (2004).

6. J. Mata, T. Joshi, D. Varade, G. Ghosh and P. Bahadur, *Colloids Surf. A.*, **247**, 1 (2004).

7. (a) M. Friedman and C. W. Sigel, *Biochemistry*, **5**, 478 (1966). (b) S. Moore and W. Stein, *J. Biol. Chem.*, **176**, 367 (1948).

Chapter-III

Micellization of Gemini Surfactants in Polar Nonaqueous-Water Mixed Solvents

Introduction

Micelle formation in nonaqueous polar solvents has attracted less attention as compared to the extensive investigations that have been reported in the literature dealing with the formation of micelles in aqueous surfactant solutions. The term "solvophobic interaction" has been coined to describe the micellization in nonaqueous polar solvents, in analogy with "hydrophobic interactions",[1] responsible for aggregation in water. However, the ability of water to form unique hydrogen-bonded networks is not a necessary condition for the aggregation process.[2] The micelles formed in nonaqueous solvents are similar in many respects to the micelles that are formed in water, although, micelle formation is not as favored in such solvents as in water for a given surfactant.[3, 4]

It is widely recognized that the cmc is the most important parameter in studies dealing with micellization of surfactants. The cmc of ionic surfactants is usually determined as the intersection point of the two straight lines in conductivity–concentration plots above and below the cmc, whereas degree of counterion dissociation of micelles, α, is determined as the ratio between the slopes of postmicellar region to that of premicellar region. [5,6] In such an analysis, the interionic interactions are ignored and conductivity is assumed to be linearly related to surfactant concentration. In addition, this procedure presents difficulties

when conductivity–concentration plots exhibit weak curvature especially observed for ionic surfactants in mixed organic solvent systems,[7] in the presence of organic additives like urea,[8] and in mixed state with the non-ionic surfactants.[9,10]

Many approaches based on differentiation of conductivity data against the surfactant concentration have been proposed[11,12] to obtain more precise cmc and α values. Such first derivative plots behave as sigmoid; the fitting of which allows evaluation of "width" of transition (the central point of transition width corresponds to the cmc value) and α. Because this procedure involves finding of numerical derivative of the experimental data as first step, it introduces numerical errors, which get amplified when joined with experimental errors, and hence lead to unavoidable errors in determination of fitted parameters. This way, the sigmoidal-like derivative shows noisy behavior (instead of a perfect and regular one).

More recently, Carpena et al.[13] have proposed an efficient method to analyze the conductivity–concentration data of ionic surfactant solutions in the context of the determination of micellization parameters viz. cmc and α. Their method is based on the fit of the experimental raw data to a simple, nonlinear function obtained by the direct integration of Boltzmann–type sigmoidal function. The method shows much better

performance than the conventional[5,6] and differential conductivity methods[11,12] for the real systems that present a very gradual transition from the premicellar to postmicellar region and in which the break in conductivity–concentration plots is hard to determine. They have shown by means of Monte Carlo simulations that the errors in the estimation of micellization parameters is smaller than by using derivative of original data in which processing of data introduces spurious errors through numerical differentiation. In addition, the effect of experimental errors on evaluation of the micellization parameters has been shown to be minimal by using this procedure.

Recently, there has been a distinct progress in research dealing with the effects of nonaqueous polar solvents on the micellization process.[4,14] Geminis have already shown promise in skin care, antibacterial regimens, construction of high–porosity material, analytical separations, and solubilization processes.[15] Scores of patents dealing with geminis have appeared in the last few years.[16] Because all practical applications of surfactants involve the presence of other species[17] such as glycols and alcohols, it is important to establish the effects of such and related compounds on micellization to explore their fundamental behavior. Survey of available literature[15,16,18] reveals that no serious attempt has been made to study the micellization phenomenon of gemini

surfactants in polar nonaqueous solvents. In this chapter, studies on the micellar properties [cmc, degree of counterion dissociation (α), and thermodynamic parameters (ΔG°_{m}, ΔH°_{m}, and ΔS°_{m})] of the gemini surfactants (16-*s*-16, s = 4, 5 or 6) in water and polar nonaqueous solvent (PrOH, MC, DMSO, AN) – water mixtures are reported.

Conductometry was used to determine the cmc and α-values. The conductivity runs were carried out by adding progressively concentrated surfactant stock solution into the thermostated solvent.

The procedure of cmc determination involves fitting of experimental conductivity data, κ, as a function of surfactant concentration, x, to the equation[13]

$$\kappa_{(x)} = \kappa_{(0)} + A_1 x + \Delta x (A_2 - A_1) \ln\left(\frac{1 + e^{(x - x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}}\right) \qquad (3.1)$$

which is integral of Boltzmann type sigmoid equation.[13] Here $\kappa_{(0)}$ represents the conductivity of solution when x = 0; A_1 and A_2 represent the pre- and postmicellar slopes, respectively; and Δx, the width of transition whose central point, x_0, corresponds to the cmc. A smaller value of Δx means abrupt transition (micellization is highly cooperative), while its higher value shows a gradual transition (micellization process is less cooperative). In the analysis, $\kappa_{(0)}$ was set equal to zero because conductivity of water was subtracted corresponding to each data point.

Data fitting was carried out by making use of initial guess values of A_1, A_2, x_0 and Δx in Eq. 3.1 to calculate an approximate value of conductivity, $^{approx.}\kappa_x$, corresponding to each surfactant concentration. Chi-square, χ^2, the sum of the squares of the deviations of approximate conductivity from the experimental values, defined as

$$\chi^2 = \sum_{i=1}^{N} [\kappa_i - {}^{approx.}\kappa_i]^2 \qquad (3.2)$$

(where N is the number of data points, κ_i and $^{approx.}\kappa_i$ the experimental conductivity and approximate conductivity at a given total surfactant concentration, respectively) was minimized with respect to these parameters and their values corresponding to the minimum were then used as the new set of guess values in an iterative procedure till χ^2 effectively stopped decreasing, indicating convergence of input and output parameters. The minimized value of χ^2 gives maximum likelihood estimate of model parameters. Eq. 3.1 being nonlinear in the parameters, a computer programme for nonlinear least squares fitting of data, as described by Press et al.[19] and making use of Levenberg-Marquardt[19] algorithm, was written with necessary modification to perform the iterative procedure for optimization of parameters. The final set of values of A_1, A_2, x_0 and Δx, when χ^2 effectively stopped decreasing, was taken as their best-fit parameters. From the ratio A_2/A_1, the degree of counterion dissociation (α) of micelles was determined following the Evan's

procedure.[20] Uncertainties in the values of cmc and α are not more than ± 0.03 x 10^{-5} mol dm^{-3} and ± 0.01, respectively.

Results and Discussion

In this study, representatives of three different classes of solvents were chosen which mainly affect the properties of background solvent medium: (1) alcohols (PrOH and MC) which mainly enhance micellization at very low mole fractions and inhibit it at higher concentrations, (2) compound that forms relatively strong hydrogen bond with water (AN), and (3) compound that is known for hydrate formation with water (DMSO).[21]

Representative plots of the conductivity vs. the bulk phase [surfactant] in aqueous solutions as well as in mixed solvents containing 10% (v/v) polar nonaqueous solvents are shown in Figs. 3.1–3.6. These data were used to obtain the cmc and α values in water and mixed solvents (Table 3.1 and Figs. 3.7 & 3.8). We can see that the cmc values of CTAB and geminis in water are in fair agreement with the published data in the literature.[22-24] Also, the α values obtained in aqueous solutions for all the geminis and the α values reported by Zana et al.[24] using the solution conductivities appear to be in good agreement.

Along with the cmc and α values in pure aqueous medium, Table 3.1 also contains the values in polar nonaqueous solvent + water mixtures (10% solvent + 90% water). The presence of 10% of the solvent in binary mixtures (with water) causes increase in cmc of all the surfactants. The inhibitory effect of the solvents (10%) for each surfactant depends upon the nature of the solvent. The behavior can be interpreted in terms of solvent interaction with water and its possible influence on solvophobic forces operating for micellization. Although each solvent postpones micellization, the reasons are quite different. In the case of PrOH or MC, the interaction consists of the destruction of the original water's 3D structure and the formation of new H-bonds between water and the alcohols.[25] These alcohol–water mixtures are better solvents for surfactants than pure water and micelles thus form at higher [surfactant]. The α values reflect the electrostatic interactions between charged micelle surfaces and counterions and, to a first approximation, is a measure of the fraction of counterions located very close to the micellar surface which is mainly affected by the surface solubilization of the alcohol. The alcohol solubilization at the micellar surface reduces the surface charge density. This effect in itself is sufficient to explain the increase of α.[25] However, such alcohol effect is not studied in literature for gemini micelles and a decrease in α (Table 3.1) in the presence of

PrOH or MC demands clarification. The presence of alcohol within the micellar interface makes water less polar that increases Coulombic interactions between headgroups and counterions with a concomitant decrease in α. However, a higher α value for 16-6-16 (Table 3.1) on the addition of PrOH or MC needs further clarification. As the spacer chain length increases, the surfactant headgroup area is reported to increase[22,26,27] with the concomitant increase in the hydration of the micelle. In case the spacer chain length is sufficiently larger, looping towards the micellar core may take place.[22,24] In either case, an increased hydration of the micelle will consequently take place. Due to this increased hydration, one can expect that the PrOH/MC may get solubilized into the headgroup region of 16-6-16 micelles (instead of being present in the interfacial region). If it is so, the solubilization effect will predominate, reducing the surface charge density and increasing α. Probably the latter effect dominates with the surfactant of higher spacer length (e.g., 16-6-16). However, this explanation needs an independent verification. The postponement of micellization in the presence of AN can also be understood in terms of the formation of hydrogen bonds between water and AN molecules. The inhibitory effect of DMSO can be explained by taking into consideration increased structuring of the H_2O–DMSO liquid system. DMSO is known to form stoichiometric hydrates with water of the type $DMSO.2H_2O$.[28] The hydrate formation

substantially restricts the motion of the surfactant molecules and reduces hydrophobic interactions with a concomitant increase in cmc (Table 3.1). However, the cmc increase is lower with DMSO in comparison to other solvents. The α values for gemini + DMSO systems follow the same trend as observed for PrOH. The presence of DMSO may cause a decrease in the overall polarity of the solvent and of α. However, an increase of α in the case of 16-6-16 + DMSO system may again be due to the solubilization effect as discussed in the case of 16-6-16 + PrOH system. Because not much data are available on gemini + nonaqueous solvent systems, further discussion on α is restricted in this study.

As the cmc increase in 16-4-16–DMSO is comparatively more with respect to water than the other gemini–DMSO combinations, to substantiate the effect, therefore, we have studied micellization phenomenon in different DMSO–water mixtures. Fig. 3.7 shows the variation of the ratio (cmc/cmc_0) of the cmc in DMSO and water mixture (cmc) to that in pure water (cmc_0) with the increasing volume percent of DMSO in DMSO–water mixtures. The data clearly demonstrate that the cmc increasing effect is much smaller in the case of 16-6-16 than the other geminis. This effect can be understood in light of the variation in the length of the spacer. The presence of a longer spacer in a gemini molecule produces greater hydrophobic interaction due to its folding

towards micellar core, hence, aggregation in highly unfavorable situation (at high DMSO volume percent). Thus, the role of the spacer chain length in the overall aggregation in DMSO–water mixture is quite distinct. However, more work is needed with other spacer chains to substantiate the point.

The thermodynamic parameters of micellization were obtained from the temperature dependence of the cmc values (Fig. 3.8). For ionic monomeric and dimeric surfactants, the relationship between the free energy of micellization per alkyl chain, ΔG°_{m}, the cmc in mole of alkyl chain per cubic decimeter, and the α values are written, respectively,[29] as:

$$\Delta G^{\circ}_{m}\,(\text{monomer}) = RT\,(2-\alpha)\,\ln \text{cmc} \qquad (3.3)$$

and $$\Delta G^{\circ}_{m}\,(\text{dimer}) = RT\,(1.5-\alpha)\,\ln \text{cmc} \qquad (3.4)$$

In Eqs. 3.3 and 3.4, the cmc is expressed in mol per cubic decimeter. In the reported literature,[26] the cmc is expressed in mole fraction unit. For surfactants with low cmc values (< 10 mM), the values of ΔG°_{m} would only differ by the constant term $\approx \ln 55.5$ when using one or the other unit.[15] The enthalpies of micellization were obtained by employing the equation

$$\Delta H^{\circ}_{m} = -RT^{2}\,(\mathrm{d}\ln \text{cmc}/\mathrm{d}T)_{P} \qquad (3.5)$$

The entropy values of micelle formation were evaluated from the calculated ΔH^{o}_{m} and ΔG^{o}_{m} values as follows:

$$\Delta S^{o}_{m} = (\Delta H^{o}_{m} - \Delta G^{o}_{m}) / T \qquad (3.6)$$

The equation employed to calculate the ΔG^{o}_{m} applies normally when the mean aggregation number is large but may not be accurate for higher concentrations of co-solvent.[30,31] As indicated by the negative values of the ΔG^{o}_{m} , it is evident that the micellization process is spontaneous in water as well as in 10% DMSO (Table 3.2). In the absence of DMSO, ΔG^{o}_{m} is nearly equal for CTAB and geminis. The low cmc values of 16-*s*-16 arise mainly because more than one chain is transferred simultaneously from background solvent to the micelle.[29,32] The ΔH^{o}_{m} values in water or water–DMSO mixtures are positive and weakly dependent on temperature within the experimental error. The enthalpy values calculated from Eq. (3.5) may differ from the directly measured calorimetric values;[33] however, we were unable to locate any data for the systems for comparison. The value of ΔS^{o}_{m}, in water become more in presence of DMSO. ΔS^{o}_{m} changes are large in comparison to water indicating that the DMSO enhances the energy of the 3D water structure due to the formation of $DMSO.2H_2O$. Because the thermodynamic parameters are dependent on both cmc and α, their values

do not show any trend, which is expected as α value has no clear-cut trend with the spacer chain length as well as with temperature. The α values were not following any trend in the earlier study also.[24] Therefore, much discussion on these parameters would not be appropriate.

In conclusion, we can say that micellization of gemini surfactants occurs in many adverse situations, such as in the presence of nonaqueous solvents which are known to arrest the phenomenon of micellization. Therefore, these systems may be utilized for the organic reactions which are occurring in polar solvents or in the presence of binary solvents whose one component is water.

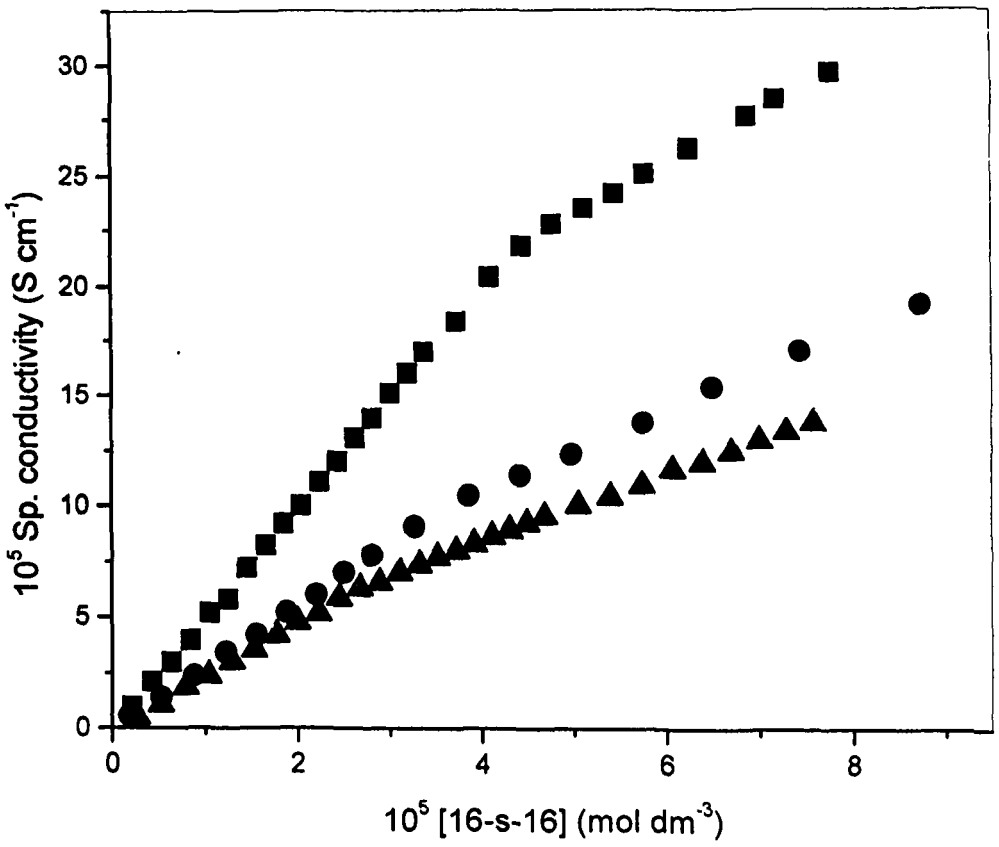


Fig. 3.1. Specific conductivities of 16–*s*–16 solutions in water as a function of surfactant concentration at 30 °C: 16-4-16 (■), 16-5-16 (●), 16-6-16 (▲).

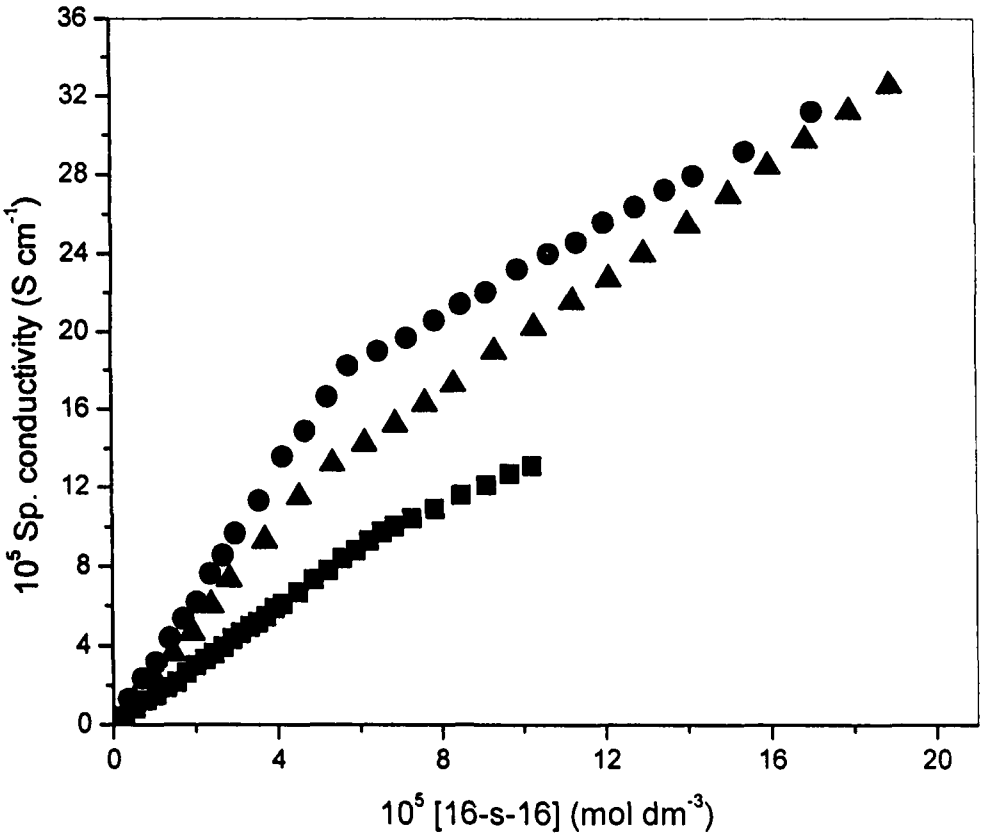


Fig. 3.2. Specific conductivities of 16–*s*–16 solutions in 10% DMSO as a function of surfactant concentration at 30 °C: 16-4-16 (■), 16-5-16 (●), 16-6-16 (▲).

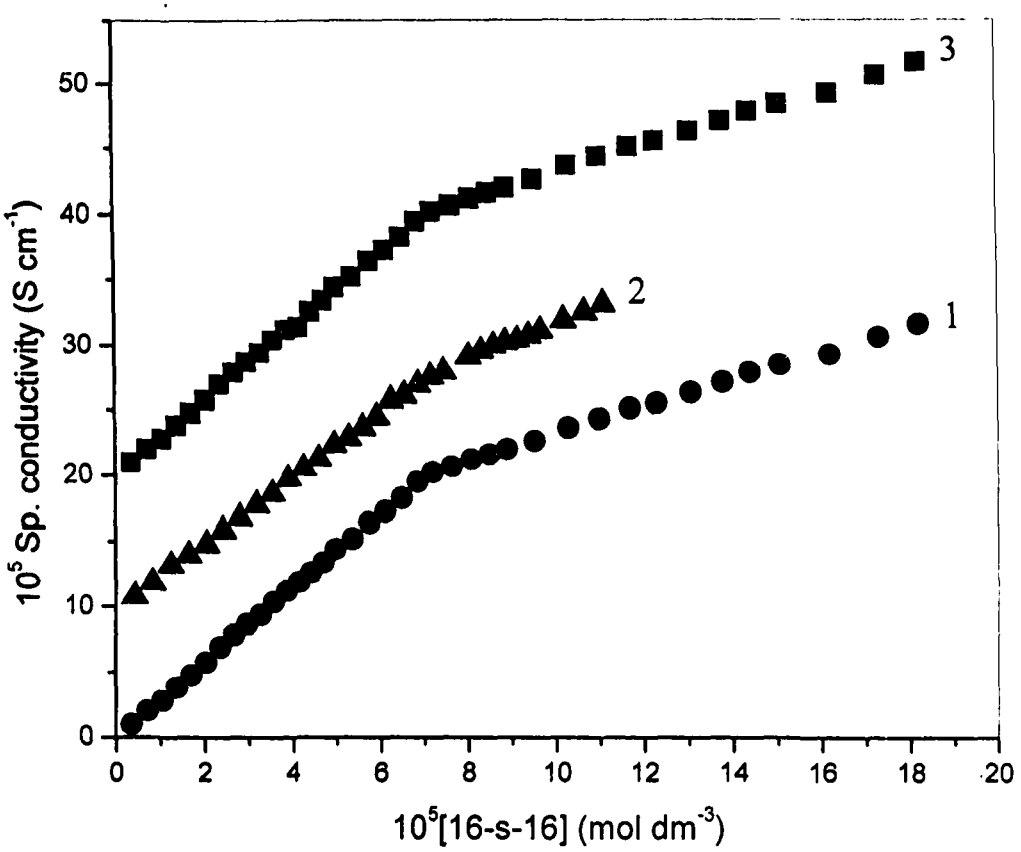


Fig. 3.3. Specific conductivities of 16–*s*–16 solutions in 10% MC as a function of surfactant concentration at 30 °C: 16-4-16 (■), 16-5-16 (●), 16-6-16 (▲). The scale shown is for curve 1. Curves 2,3 have been shifted upwards by 10, 20 scale units ($1x10^{-5}$ S cm^{-1}), respectively.

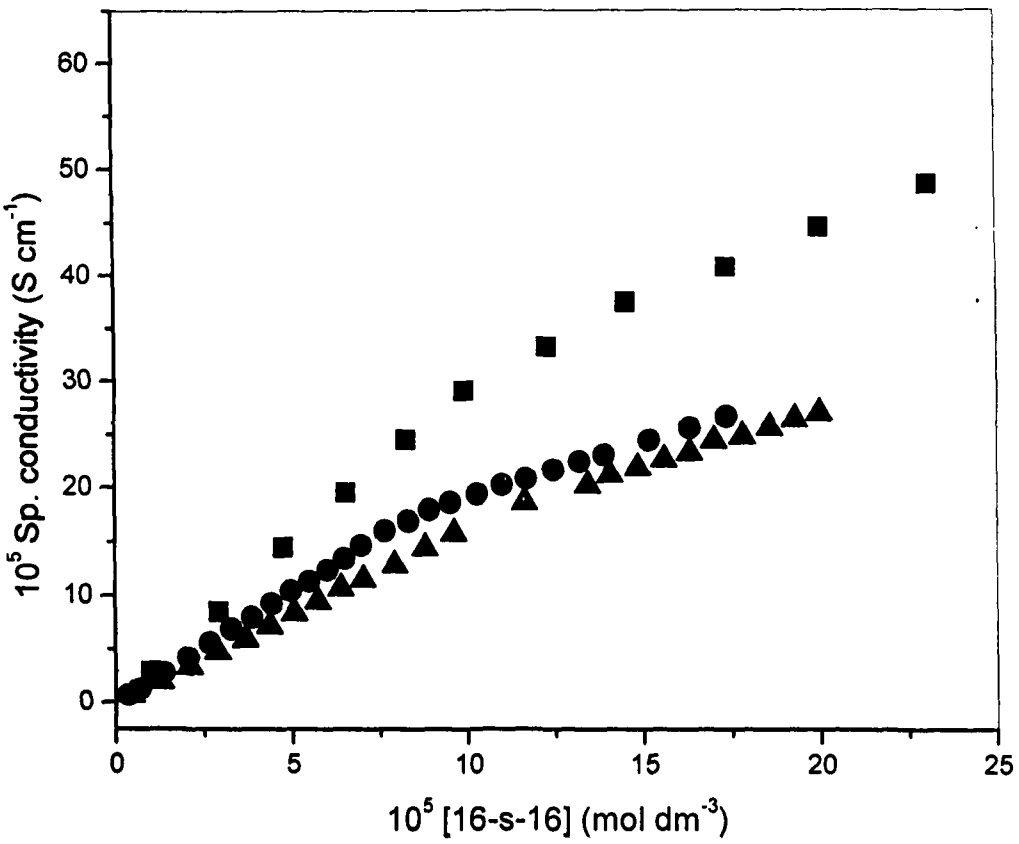


Fig. 3.4. Specific conductivities of 16–*s*–16 solutions in 10% PrOH as a function of surfactant concentration at 30 °C: 16-4-16 (■), 16-5-16 (●), 16-6-16 (▲).

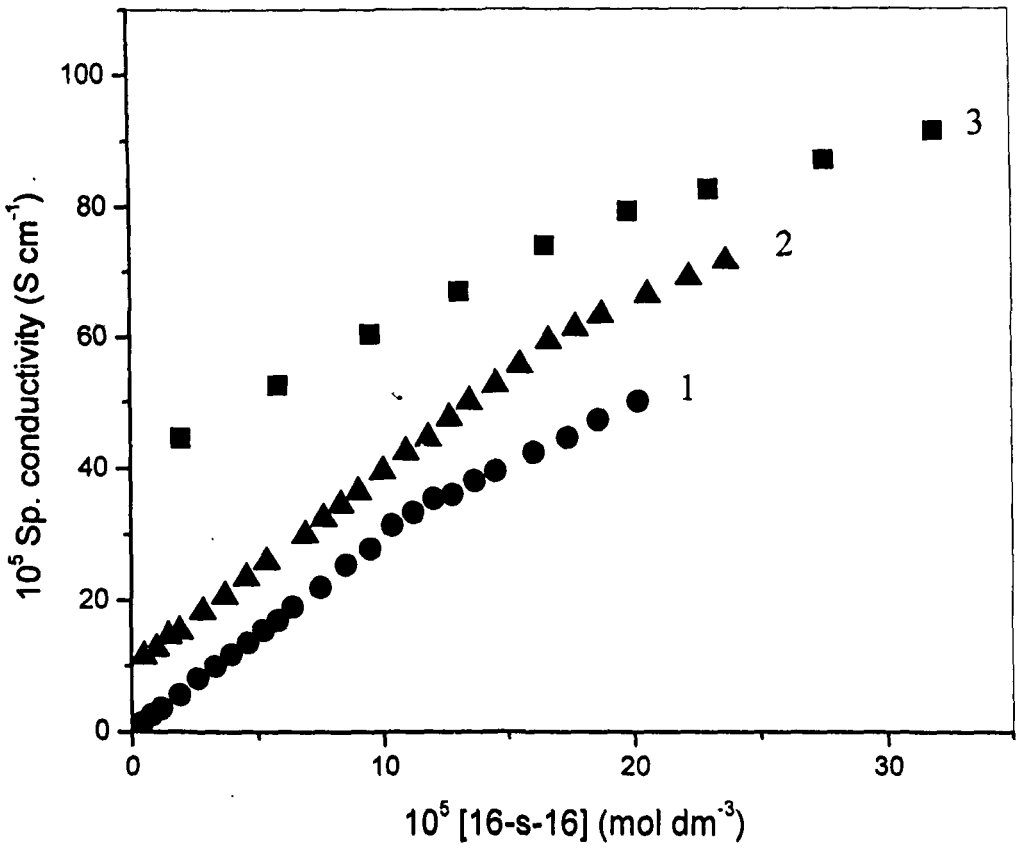


Fig. 3.5. Specific conductivities of 16–*s*–16 solutions in 10% AN as a function of surfactant concentration at 30 °C: 16-4-16 (■), 16-5-16 (●), 16-6-16 (▲).The scale shown is for curve 1. Curves 2,3 have been shifted upwards by 10, 40 scale units ($1x10^{-5}$ S cm^{-1}), respectively.

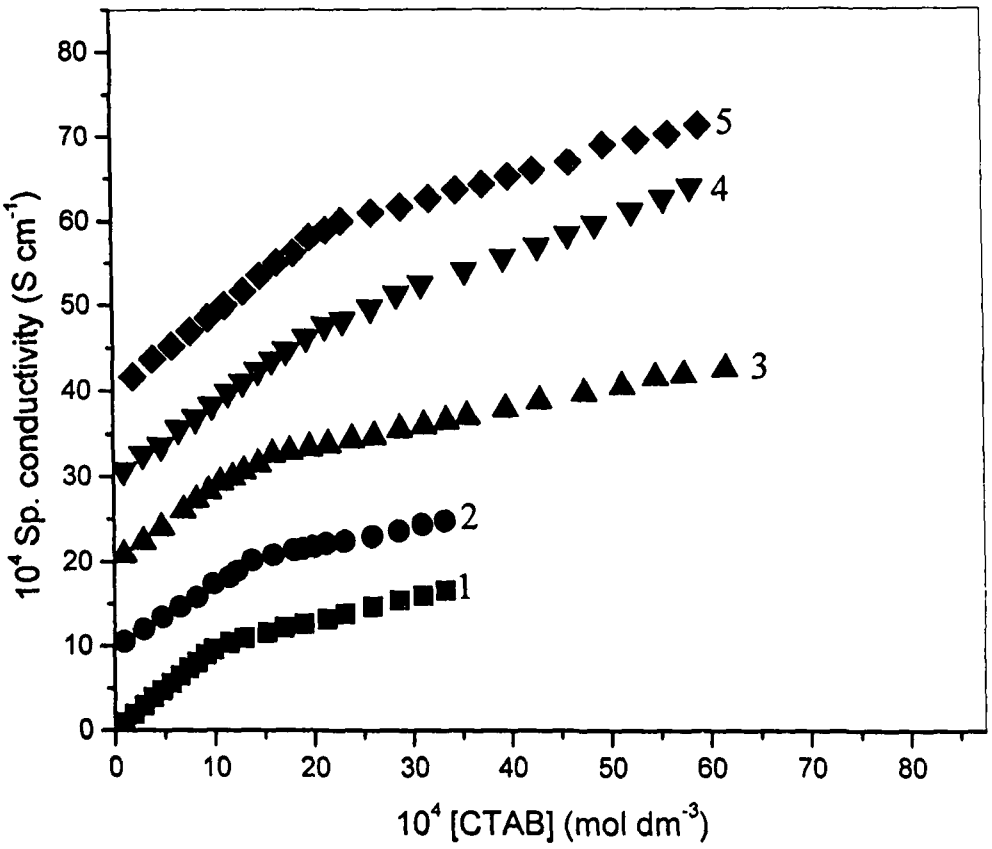


Fig. 3.6. Specific conductivities of CTAB solutions in the presence of different solvents as a function of surfactant concentration at 30 °C: water (■), MC (●), DMSO (▲), PrOH (▼) and AN (◆).The scale shown is for curve 1. Curves 2,3,4,5 have been shifted upwards by 10,20,30,40 scale units ($1x10^{-5}$ S cm^{-1}), respectively.

Table 3.1: cmc and α values of surfactants in polar nonaqueous-water mixed solvents (10% : 90% v/v) at 30 °C.

Surfactant	H_2O		PrOH		MC		DMSO		AN	
	cmc x10^5 (mol dm^{-3})	α	cmc x10^5 (mol dm^{-3})	α	cmc x10^5 (mol dm^{-3})	α	cmc x10^5 (mol dm^{-3})	α	cmc x10^5 (mol dm^{-3})	α
16-4-16	2.83	0.64	10.62	0.44	9.92	0.43	6.5	0.63	18.42	0.41
16-5-16	3.63	0.67	8.39	0.49	7.08	0.35	5.67	0.36	11.32	0.62
16-6-16	4.37	0.47	10.75	0.62	7.38	0.55	5.49	0.65	17.10	0.58
CTAB	100.54	0.29	205.38	0.52	152.80	0.36	154.42	0.27	218.04	0.34

Uncertainties on cmc and α are estimated to be less or equal to $\pm$ 0.03x 10^{-5} mol dm^{-3} and $\pm$ 0.01, respectively

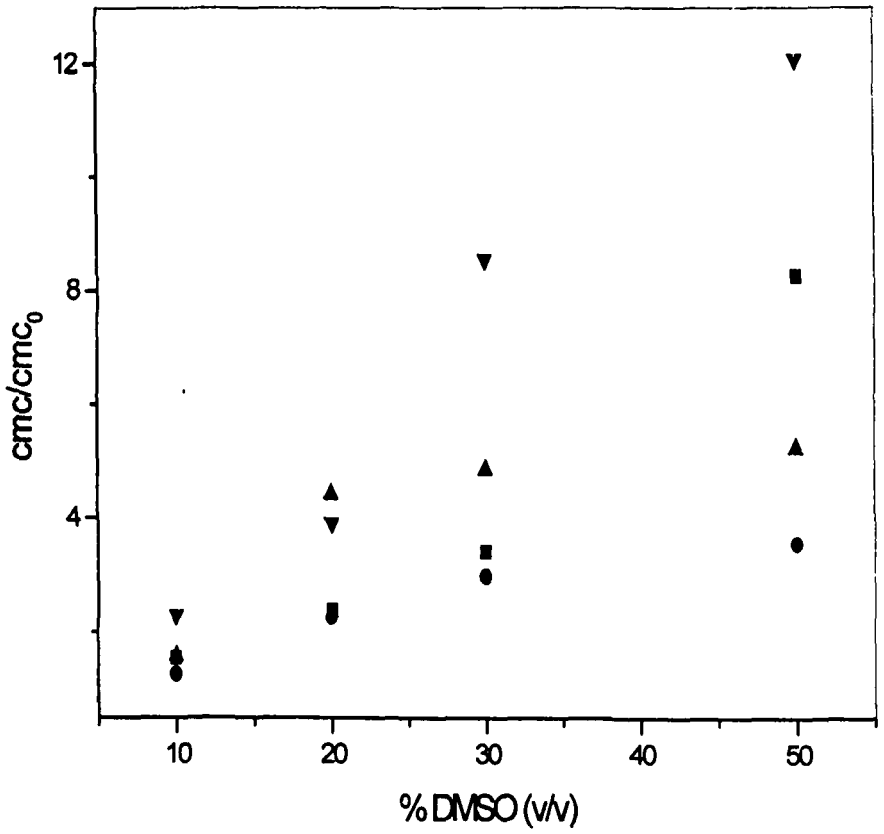


Fig. 3.7. Variation of cmc ratio (cmc/cmc_0) of different surfactants as a function of volume percent of DMSO in DMSO-water mixed solvent: CTAB (■), 16-4-16 (▼), 16-5-16 (▲), 16-6-16 (●).

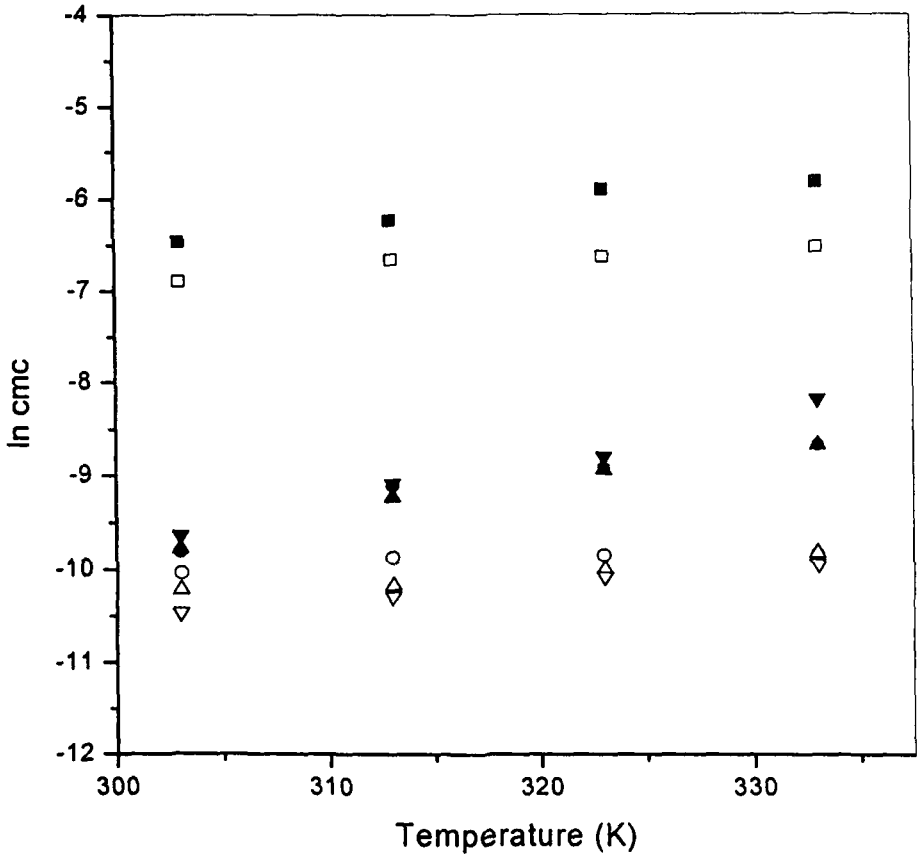


Fig. 3.8. Variation of ln cmc with temperature: CTAB (□,■), 16-4-16 (▽, ▼), 16-5-16 (Δ,▲), 16-6-16 (○,●) (open symbols are for water while closed symbols are for 10% DMSO-water mixtures).

Table 3.2: Thermodynamic parameters of micellization of different surfactants in water and DMSO-water mixture.

% DMSO (v/v)	Temp. (°C)	16-6-16			16-5-16		
		ΔG°_m (kJmol^{-1})	ΔH°_m (kJmol^{-1})	ΔS°_m (JK^{-1}mol^{-1})	ΔG°_m (kJmol^{-1})	ΔH°_m (kJmol^{-1})	ΔS°_m (JK^{-1}mol^{-1})
0	30	-26.03	12.97	128.71	-21.36	12.21	110.79
	40	-21.56	13.84	113.10	-25.05	13.03	121.66
	50	-23.53	14.74	118.48	-25.41	13.87	121.61
	60	-18.79	15.67	103.48	-21.74	14.74	109.55
10	30	-20.99	27.47	159.95	-28.07	29.75	190.83
	40	-25.59	29.31	175.39	-26.41	31.75	185.81
	50	-23.46	31.21	169.26	-27.60	33.81	190.11
	60	-26.39	33.17	178.86	-26.15	35.94	186.46

Contd...

		16-4-16			CTAB		
0	30	-22.67	14.50	122.67	-29.71	11.90	137.33
	40	-26.50	15.47	134.09	-28.41	12.70	131.34
	50	-27.06	16.47	134.77	-28.83	13.52	131.11
	60	-26.68	17.51	132.70	-27.24	14.38	124.98
10	30	-21.12	35.86	188.04	-28.18	20.60	160.99
	40	-25.30	38.26	203.06	-26.90	21.98	156.17
	50	-26.91	40.75	209.50	-28.82	23.41	161.70
	60	-24.66	43.31	204.11	-23.67	24.88	145.80

References

1. C. Tanford, *"The Hydrophobic Effect: Formation of Micelles and Biological Membranes"*, 2nd ed., Wiley, New York (1980).

2. A. Beesley, D. F. Evans and R. G. Laughlin, *J. Phys. Chem.*, **92**, 797 (1998).

3. A. Ray, *J. Am. Chem. Soc.*, **91**, 6511 (1969).

4. T. Perche, X. Auvray, C. Petipas, R. Anthore, E. Perez, I. Rico-Lattes, and A. Lattes, *Langmuir*, **12**, 863 (1996).

5. R. Zana, H. Levy, D. Danino, Y. Talmon and K. Kwetkat, *Langmuir*, **13**, 402 (1997).

6. M. Perez Rodriguez, G. Prieto, C. Rega, L. M. Varela, F. Sarmiento, and V. Mosquera, *Langmuir*, **14**, 4422 (1998).

7. C. C. Ruiz, *Colloid Polym. Sci.*, **277**, 701 (1999)

8. C. C. Ruiz, *Colloids Surf. A*, **147**, 349 (1999).

9. K. P. Jana and S. P. Moulik, *J. Phys. Chem.*, **95**, 9525 (1991).

10. A. D. Burman, T. Dey, B. Mukherjee and A. R. Das, *Langmuir*, **16**, 10020 (2000).

11. M. Manabe, H. Kawamura, A. Yamashita and S. Tokunaga, *J. Colloid Interface Sci.*, **115**, 147 (1987).

12. G. Sugihara, Y. Era, M. Funatsu, T. Kunitaka, S. Lee and Y. Sasaki, *J. Colloid Interface Sci.*, **187**, 435 (1997).

13. P. Carpena, J. Aguiar, P. Bernaola-Galvan and C. C. Ruiz, *Langmuir*, **18**, 6054 (2002).

14. (a) T. Warnheim, *Curr. Opin. Colloid Interface Sci.*, **2**, 472 (1997). (b) R. Zana, *Colloids Surf. A*, **123**, 27 (1997) (c) C. C. Ruiz, *J. Colloid Interface Sci.*, **221**, 262 (2000).

15. R. Zana, *Adv. Colloid Interface Sci.*, **97**, 205 (2002).

16. M. J. Rosen and D. J. Tracy, *J. Surf. Detergents*, **1**, 547 (1998).

17. P. D. Sawant, B. K. Mishra and C. Manohar, *Langmuir*, **10**, 3485 (1994).

18. F. M. Menger and J. S. Keiper, *Angew. Chem. Int. Ed.*, **39**, 1906 (2000).

19. W. H. Press, S. A. Teukolsky, W. T. Vellerling and B. P. Flammer, "*Numerical Recipes in Fortran*", Oxford University Press, Chapter 15 (1992).

20. H. C. Evans, *J. Chem. Soc.*, 579 (1956).

21. L. G. Ionescu, L. S. Romanesco and F. Nome, *"Surfactants in Solution"*, Edited by K. L. Mittal and B. Lindman, Plenum Press, New York, Vol. 2 (1984).

22. S. De, V. K. Aswal, P. S. Goyal and S. Bhattacharya, *J. Phys. Chem.*, **100**, 11664 (1996).

23. P. Mukerjee and K. J. Mysel, *"Critical Micelle Concentrations of Aqueous Surfactant Systems"*, NSRDS-NBS 36, Superintendent of Documents, Washington, D.C. (1971).

24. R. Zana, M. Benrraou and R. Rueff, *Langmuir*, 7, 1072 (1991).

25. R. Zana, *Adv. Colloid Interface Sci.*, **57**, 1 (1995).

26. E. Alami, G. Beinert, P. Marie and R. Zana, *Langmuir*, **9**, 1465 (1993).

27. H. Diamant and D. Andelman, *Langmuir*, **10**, 2910 (1994).

28. L. G. Ionescu and E. F. de Souza, *"Surfactants in Solution"*, Edited by K. L. Mittal and A. K. Chattopadhyay, Marcel Dekker, New York, Vol. 64 (1996).

29. T. A. Camesano and R. Nagarajan, *Colloids Surf.*, **167**, 165 (2000).

30. C. C. Ruiz, J. A. Molina-Bolivar and J. Aguiar, *Langmuir*, **17**, 6831 (2001).

31. D. Attwood and A. T. Florence, "*Surfactant Systems, their Chemistry, Pharmacy and Biology*", Chapman and Hall, London (1983).

32. R. Zana, *Langmuir*, **12**, 1208 (1996).

33. J. M.del Rio, G. Prieto, F. Sarmiento and V. Mosquera, *Langmuir*, **11**, 1511 (1995).

Chapter-IV

Viscometric and Dynamic Light Scattering Studies on Aqueous Gemini Surfactants in Presence of Additives

Introduction

Conventional (monomeric) surfactant molecules contain a hydrophobic chain and a hydrophilic headgroup. In solutions, they form a variety of aggregates with properties different from those of the unassembled molecules. The morphologies and dynamics of aggregates formed by surfactant molecules (spherical micelles, rodlike micelles, bilayers, reverse micelles) are known to influence strongly the performance properties spanning biology, household cleaning and soil cleanup. As of today, in most of their applications, surfactants with additives, rather than pure, are preferred. As such systems often exhibit exceptional properties through synergism,[1-6] studying the properties of surfactant–additive systems would, therefore, be of great relevance to cope with the ever–increasing demand of surfactant systems for life's diverse fields. In this direction, Kabir-ud-Din and his group have been involved in studying the effect of a variety of additives (salts, denaturants, cosurfactants, hydrocarbons, aromatic acids, etc.) on the solution (consolute behavior) and association properties (micellization, sphere-to-rod transition (s→r), micellar growth/destabilization) of monomeric surfactant systems using viscometry, cloud point measurement, small-angle neutron scattering (SANS), dynamic light scattering (DLS),[7–17] etc. The findings of the study involved two new problems: (i) "is there any synergism when additives are present

simultaneously", and (ii) "can an additive be used as an effective 'weapon' to produce synergism in a surfactant system?" It has been demonstrated that the viscosity increased with the increase of [additive] and that the magnitude of viscosity was substantial when organic additives were added in the presence of an inorganic salt. Surfactant solutions containing spherical micelles are of isotropic nature and of low viscosity[18] whereas, presence of rod-shaped micelles imparts higher viscosity to the solution.[19-22] Thus, viscosity can also be used to study structural transitions in the surfactant solutions (e.g., s→r). The findings based on viscosity results were well supported by SANS [7,9,10] and DLS measurements.[15,16]

A vast majority of experimental data are available on solution/aggregational behavior of conventional surfactants in presence of different class of additives. However, this is not the case with the gemini surfactants. All the generalization of conventional surfactants are not followed by geminis, e.g., cmc's can be higher for longer chain geminis than for shorter chain counterparts (just the reverse of normal conventional case).[23] Studies of solubilization of organic compounds in gemini micellar solutions are still scarce.[24,25] Addition of KBr to a solution of gemini surfactant brought about the formation of a lamellar phase followed by phase separation.[26] Apart from above scanty reports, no systematic attempt has been made to study the effect of additives on

gemini micellar solutions. To our knowledge, this is entirely a new area of research on gemini surfactants. In the present study, the viscometric and dynamic light scattering (DLS) measurements have been performed on the dimeric gemini–additive systems to see the role of organic additives (alcohols, C_4–C_6OH and hexylamine, C_6NH_2) in the absence and presence of KBr toward micellar growth. Recent studies of microscopic aggregate structures by DLS coupled with viscometry highlight important links between structure and bulk physical properties.[16] Thus, to provide additional evidence regarding the effect of additives on the transition of gemini micelles, both viscosity and DLS measurements were carried out simultaneously on the chosen systems in the presence of different additives.

The technique of dynamic light scattering (DLS) is one of the most popular methods used to determine the size of particles, from which we can see the shapes of various self-organizing systems. Consequently, we examined how a specific series of dimeric micelles adopt different morphologies in aqueous media depending on the spacer chain length(s) using DLS experiments. Measurements were also performed with a conventional surfactant (cetyltrimethylammonium bromide, CTAB) for comparison purposes.

Viscometry: Fluids consist of molecular layers which are arranged one over the other. It flows, when a shearing force is applied to a liquid. However, the frictional forces between the layers offer resistance to this flow. Viscosity of a liquid is a measure of its frictional resistance. Viscosity is expressed as dyne-seconds cm^{-2} or poise. Generally smaller units, centipoise and millipoise are used.

Viscosity of a liquid can be determined with the help of Poiseuille's equation which governs the flow of a liquid through a capillary. If l is the length of the capillary, r its radius, p the pressure difference at the ends, and v

the volume flowing per second through the capillary, then η the coefficient of viscosity is given by

$$\eta = \pi r^4 pt / 8l\, v \qquad (4.1)$$

It is not possible to find the absolute coefficient of viscosity (η) straight away from Poiseuille's equation as experimental measurement of p, r, l and v offers considerable difficulty.

Hence viscosity of a liquid is determined with respect to another liquid, usually water. This is called relative viscosity.

Let t_1 and t_2 be the times of flow of a fixed volume of two liquids through the same capillary. The expression for relative viscosity (η_r) is given by

$$\eta_r = \eta_1 / \eta_2 = (\pi r^4 p_1 t_1 / 8l\, v) \times (8l\, v / \pi r^4 p_2 t_2) \qquad (4.2)$$

Since the pressure is proportional to the density, we have

$$\eta_r = d_1 t_1 / d_2 t_2 \tag{4.3}$$

where d_1 and d_2 are the densities of the solution and solvent. Ozeki and Ikeda[27] found density corrections to be negligible, η_r values may, therefore, be calculated using Eq. (4.4)

$$\eta_r = t_1 / t_2 \tag{4.4}$$

Dynamic Light Scattering (DLS). The Stokes-Einstein formula, Eq. (4.5), is commonly used to describe the relationship between the diffusion coefficient D and the hydrodynamic radius R_h of dilute, neutral monodisperse spherical particles in solution:

$$D = k_B T / 6\pi\eta R_h \tag{4.5}$$

where k_B is the Boltzmann constant and η is the viscosity of the solvent at absolute temperature T. To obtain the length (L) of the rod, we have used the simple formula for the radius of gyration for a rod,

$$R_g^2 = (R^2/2) + L^2/12 \tag{4.6}$$

where $R_g = \sqrt{3}/5\ R_h$ for sphere, and R was taken as the chain length of surfactant. R_h values were used to obtain hydrodynamic diameter (D_h).

Dynamic light scattering measures a time profile of the normalized autocorrelation function of the light intensity, $g^{(2)}(t)$, which is related to the electric field normalized correlation function, $g^{(1)}(t)$, through the Siegert relation[28] :

$$g^{(2)}(t) = 1 + \beta \left| g^{(1)}(t) \right|^2 \tag{4.7}$$

where β is the coherence factor ($0 < \beta \leq 1$). $g^{(1)}(t)$ can be written as the Laplace transform of the distribution of the relaxation rates, $G(\Gamma)$:

$$g^{(1)}(t) = \int^{\infty} G(\Gamma) \exp(-\Gamma t)\, d\Gamma \qquad (4.8)$$

where Γ is the relaxation rate. For relaxation times, τ, $g^{(1)}(t)$ will be expressed as

$$g^{(1)}(t) = \int^{\infty} A(\tau) \exp(-t/\tau)\, d\tau \qquad (4.9)$$

where $\tau A(\tau) \equiv \Gamma G(\Gamma)$. The diffusion coefficient, D, was calculated from Γ, according to the equation,

$$D = \Gamma / Q^2 \qquad (4.10)$$

To obtain $\tau A(\tau)$, DLS data were analyzed using the CONTIN method.[29] The relaxation rates gave distributions of the diffusion coefficients and, hence, of the hydrodynamic radius (R_h) via the Stokes–Einstein equation. From this equation we can also get the values of hydrodynamic diameter ($D_h = 2x\ R_h$).

Results and Discussion

There are at least two opposing factors responsible for the micellar growth process. One is the electrostatic repulsion term originating from intermicellar and intramicellar Coulombic interactions that favors micelles with a high surface area per headgroup, that is, spherical micelles. The other is due to the hydrophobic interactions between the hydrocarbon part of the micelles/monomers, which try to achieve aggregates with tightly packed chains, that is, rods or disks. The structural transition is accompanied by a distinct rise in viscosity (Figs. 4.1–4.11 (a)), which can be correlated with the present D_h variation with different additive systems. Mukerjee[30] had proposed that an additive that is surface active to a hydrocarbon–water interface will be mainly solubilized at the micellar surface and will promote micellar growth.

Fig. 4.1 (a), shows the variation of relative viscosity ($\eta_r = \eta/\eta_0$, η and η_0 represent the viscosities of surfactant solution and solvent water, respectively) with surfactant concentration whereas plots of the variation of hydrodynamic diameter, D_h, with surfactant concentration are shown in Fig. 4.1(b). These plots were used to obtain the surfactant concentration needed to explore the effect of additives in detail. We can see that the values of η_r as well as D_h increase with the increasing surfactant concentration in each case, but, as compared to CTAB, the increase is much pronounced in the case of geminis. Further, within geminis, η_r and

D_h are found to vary with s: one can easily conclude that the size of the micelles is not the same even when they have identical concentrations. Higher values of η_r and D_h with smaller spacer chain reflect the ability of gemini surfactants of short spacers to give rise to rod-shaped micelles at fairly low concentration.[31] These findings are consistent with the earlier observation by Zana and co-workers[32,33] with dimeric surfactants with short spacers having a very strong propensity for micellar growth and formation of micelles of very low curvature. From the data shown in (Tables 4.1 (a & b) Figs. 4.1 (a & b)), we can see the s-to-r transition concentration increases with s, which may be due to a steric effect caused by an increasing flexibility of the s bridge. An increasing flexibility may permit a closer approach of the two ammonium headgroups of the surfactant molecule. Alternatively, a longer bridge can maintain both ammonium groups separated and then reduce the tendency to transform a sphere into a rod. From these figures, a concentration (0.03 M) was chosen, which was fixed for studying further the effect of additives in the gemini micellar media.

To see the effect of inorganic salt KBr, values of η_r and D_h were obtained with increasing concentration of KBr in 0.03 M fixed concentration of all of the surfactants (geminis and CTAB) at 30 °C (Tables 4.2 (a & b), Figs. 4.2 (a & b)). The presence of KBr ions near the polar heads of the surfactant molecules decreases the repulsion force

between the headgroups. This reduction in the repulsion makes it possible for the surfactant molecules to approach each other more closely and form larger aggregates, which requires much more space for the hydrophobic chains. As already mentioned, there are at least two factors responsible for determining such a change in the presence of KBr. One is the electrostatic effect of KBr due to the counterion binding on ionic micelles, and the other is the hydrophobic interaction between surfactant molecules caused by the change in the hydrogen bonded structure of water. It is clearly indicated from Figs. 4.2 (a & b) that there is steep rise in the values of η_r and D_h in the 0.03 M concentration of gemini micelles. Here again micellar growth is much higher in 16–4–16 than when $\dot{s} = 5$ or 6., which is in conformity with the earlier findings of Buhler et al.[26] At 0.03 M CTAB, there is hardly any change in the viscosity or hydrodynamic diameter (D_h) of micelles, and hence we can say that there is no micellar growth observed at this concentration of CTAB. In this case micelle growth is detected only at concentrations above 0.2 M in the absence of salt, or at lower surfactant concentrations in the presence of KBr.[32]

In contrast to conventional surfactants, where the headgroups are randomly distributed on the surface separating the aqueous phase and the micelle hydrophobic core and the distribution of distances between headgroups are maximum at a thermodynamic equilibrium distance

determined by the opposite forces involved for micellization, in gemini surfactants the distribution becomes bimodal.[34] The bimodal distribution of headgroup distances and effect of chemical link between the headgroups on the packing of surfactant alkyl chains are expected to strongly affect the curvature of the surfactant layer, and thus the micelle shape and the properties of the solutions. Therefore, salt addition would influence this distribution (and also optimum area per headgroup (A_o) with a concomitant increase in the Mitchell-Ninham parameter,[35] R_P ($v_c/A_o l_c$, v and l_c are, respectively, the volume and length of the surfactant monomer)). This is mainly responsible for a drastic change in the size of the micelle and viscosity of the solution. From these variations concentrations of KBr was chosen, i. e., 0.001 M for $s = 4$, and 0.005 M for $s = 5, 6$, which was further used to see the synergistic effects.

To see the effect of alcohols, the variations of η_r and D_h with [alcohol] for the three gemini surfactants are depicted in Tables 4.3–4.5 (a & b), Figs. 4.3–4.5 (a & b). The effects of solubilized alcohols are dependent upon their alkyl (hydrophobic) group. Short alkyl chain alcohol (C_4OH) has not much effect on the micelle size and the aggregation number. It is due to the fact that primary alcohols with short alkyl chain inhibit the surfactant molecules from penetrating into the micelles.[36] On the other hand, addition of alcohols C_5OH or C_6OH increases the micelle size by producing relatively large alcohol–surfactant

mixed micelles.[20] The difference in the solubilization mechanisms on the micellar surfaces can be confirmed by measuring the distribution coefficient, that is, the ratio of the fraction of alcohols in the micellar core side to water in the bulk phase. The large distribution coefficient implies that the alcohol–gemini mixed micelles form easily, and thus the micelle size and the shape transition are enhanced by the presence of the alcohols. It is obvious from the data that lower chain length alcohol C_4OH shows only a marginal effect on the size of the micelles. This may be because C_4OH is a hydrophilic molecule with significant solubility in water and less in micelles. Thus, it will not affect micellar structure appreciably, and in this way no significant change in the viscosity or hydrodynamic diameter of 0.03 M 16–*s*–16 is observed. As is clear by Figs. 4.3–4.5 (a & b), the addition of longer chain alcohols has indeed produced rod-shaped micelles with increased micellar size.[37] These alcohols are more likely to get embedded between monomers comprising a micelle. Because of this penetration of a surfactant-rich film between the similarly charged headgroups, the headgroup repulsion is minimized. As a result, there is a decrease in surface area occupied per headgroup (A_o). Consequently, R_P increases. An increase in this parameter could be understood by considering 16–*s*–16-higher chain length additive couple as a *single-surfactant*. Hence, the volume of the micellar core will increase because of this penetration, which is equivalent to increasing v_c.[38] This

seems to result in an increase in R_P value. Therefore, 16-*s*-16-higher chain length additives should have a tendency to form large micelles, and it seems to do so as reflected by the rise in η_r and D_h on addition of higher alcohols (C_5OH, C_6OH) and amine (C_6NH_2) to 0.03 M 16–*s*–16 micellar solutions (Figs. 4.3–4.5 (a & b) and 4.9–4.11 (a & b)). Further, R_P would be higher with increasing chain length of alcohols in the following order: C_6OH > C_5OH > C_4OH. This is due to the increasing hydrophobic volume, which would increase R_p more with concomitant formation of larger micelles (higher viscosity and D_h values). Hartel and Hoffman[39] used such arguments to design lyotropic nematics.

The combined effect of salt (0.001/0.005 M KBr) and alcohol (C_4–C_6OH) additions on 16–*s*–16 micelles is shown in Figs. 4.6–4.8 (a & b) & Tables 4.6–4.8 (a & b). These plots are the clear evidence for the growth processes due to the combined presence of KBr and organic additive. This shows that a novel phenomenon exists when salt and organic additives both are present in the micellar solution. The manifold increase in the η_r and D_h values is the result of variation of different forces responsible for micellar growth. Addition of KBr to the 16–*s*–16 micelles weakens the Coulombic repulsion between the micelles, and interaction of organic additives decreases the intramicellar Coulombic repulsive forces and increases hydrophobic interactions among monomers of the 16–*s*–16 micelle. As already discussed, the decrease of Coulombic

repulsion and/or increase in hydrophobic interactions are favorable conditions for micellar growth (either one of which exists when 0.001/0.005 M KBr or organic additive is present singly).

The addition of C_6NH_2 causes a similar increase in η_r and D_h with increasing [C_6NH_2], but at higher [C_6NH_2] these values reach near constancy (rather a decrease, Figs. 4.9–4.11 (a & b)). This different behavior can be interpreted in terms of its partitioning in aqueous phase, which affects the water structure and causes some sort of destabilization of the micelle. Because of partitioning, interfacial content of C_6NH_2 would increase the size of the micelles, while aqueous partitioning of C_6NH_2 would decrease the size. These two opposite tendencies may impart a near constancy (or even a decrease) to the η_r as well as D_h values at higher [C_6NH_2] (Tables 4.9 & 4.10 (a & b) and Figs. 4.9–4.11(a & b)).

Figs. 4.9–4.11 (a & b) also show that for equal chain lengths, the growth (high η_r and D_h values) is more with hexanol than with hexylamine. It was reported earlier that C_4–C_{10} *n*- alkylamines are solubilized in ionic micelles by electrostatic and hydrophobic effects with the amine group left on the surface of the micelle.[40] Their partial dissociation into $-NH_3^+$ and OH^- (although feebly) may affect electrostatic interactions with cationic headgroup of 16–*s*–16 micelles, which decreases the partitioning content of C_6NH_2 in the headgroup region. It has already been reported that interfacial partitoning

content (IPC) of the organic additives plays an important role toward micellar growth.[11,12] Therefore, the decrease in effective C_6NH_2 content at the micellar surface hinders the micellar growth, and thus comparatively lower values of η_r and D_h result (Tables 4.9 & 4.10 (a & b) & Figs. 4.9–4.11).

Data on the effect of adding alcohols in 0.03 M 16–*s*–16 solutions in the presence of 0.001/0.005 M KBr obtained from the two different methods are compared in Figs. 4.12–4.14 (a & b). The figures illustrate that the two types of measurements provide nearly the same value at which s→r transitions take place, thus confirming the validity of the two data sets.

It can be concluded that with respect to the corresponding monomeric surfactant cetyltrimethylammonium bromide (CTAB), dimeric surfactants have been found to have a much stronger tendency for micellar growth. Addition of a general ionic salt KBr plays a role in weakening electrostatic repulsions between the gemini micelle cationic headgroups and thereby induces the structural changes from spherical to rodlike or disklike shape. The presence of primary alcohols (butanol, pentanol, hexanol) enhances the sphere-to-rod transition and reduces the threshold concentration for the onset. This is due to the formation of the gemini–alcohol mixed micelles. Thus, the micellar size is larger in the presence of alcohols as confirmed by viscometry and DLS techniques.

The alcohols progressively get embedded between the monomers of the micelle, which increases the volume of the micellar core. Thus, longer alkyl chain alcohols form efficiently larger micelles. A combined presence of KBr and alcohols or *n*-hexylamine shows a synergistic effect on the size of the 16–*s*–16 micellar solutions, which produce favorable conditions for micellar growth that do not exist in the presence of either the salt or additive alone. For additives of equal chain length of alcohol and amine (C_6OH and C_6NH_2), the alcohol is found more effective for cationic gemini micellar growth.

Table 4.1 (a): Variation of relative viscosity (η_r) with the surfactant concentration at 30 °C.

[16-4-16]	η_r	[16-5-16]	η_r	[16-6-16]	η_r	[CTAB]	η_r
0	1.00	0	1.00	0	1.00	0	1.00
0.004	1.07	0.0100	1.12	0.01	1.10	0.030	1.09
0.008	1.12	0.0150	1.18	0.02	1.16	0.050	1.18
0.010	1.15	0.0200	1.28	0.03	1.27	0.075	1.26
0.012	1.20	0.0270	1.29	0.04	1.29	0.100	1.34
0.016	1.27	0.0300	1.30	0.05	1.30	0.150	1.56
0.020	1.42	0.0350	1.30	0.06	1.40	0.175	1.71
0.025	1.50	0.0375	1.38	0.07	1.54	0.200	1.92
0.027	1.55	0.0450	1.76	0.08	1.79	0.225	2.08
0.030	1.74	0.0500	2.57	0.09	2.24	0.250	2.33
0.035	1.85		turbid	0.10	3.41	0.300	3.14
0.040	2.32				turbid		turbid
0.050	3.35						
0.060	3.90						
	turbid						

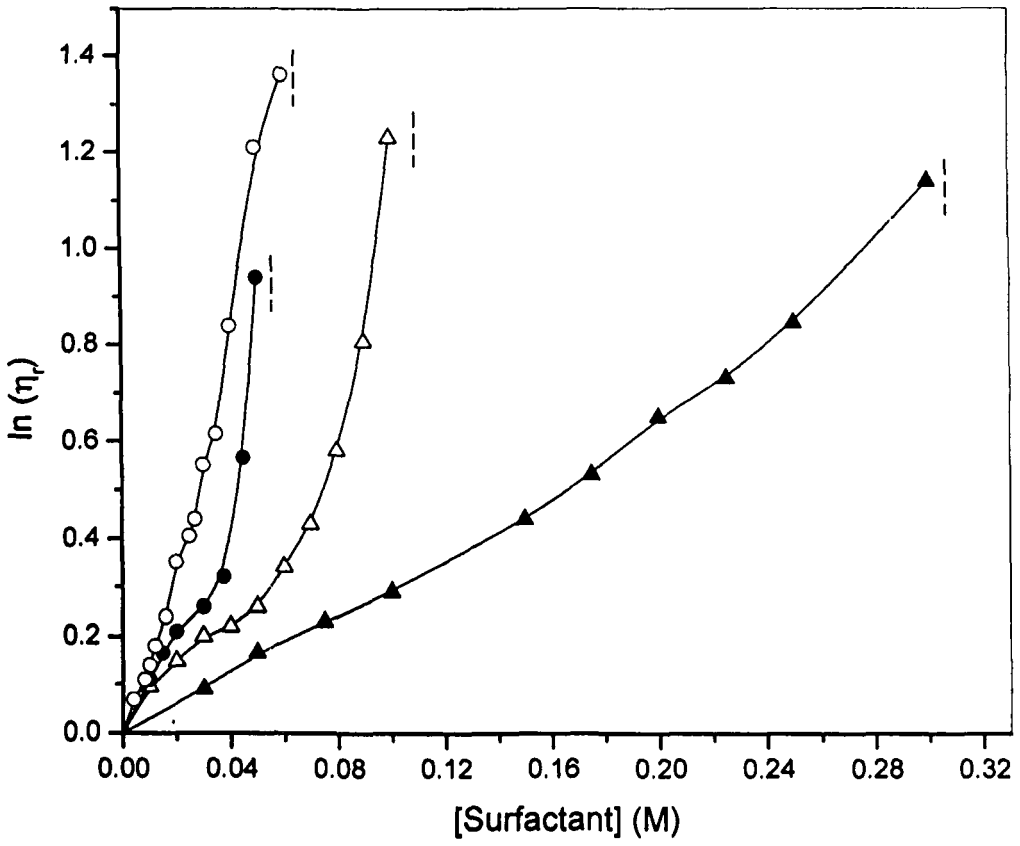


Fig. 4.1(a) Variation of ln (η_r) with the [surfactant] at 30 °C (upto the solubility limit indicated by dotted lines): 16–4–16 (○); 16–5–16 (●); 16–6–16 (Δ); CTAB (▲).

Table 4.1 (b): Variation of hydrodynamic diameter (D_h) with the surfactant concentration at 30 °C.

[16-4-16]	D_h (nm)	[16-5-16]	D_h (nm)	[16-6-16]	D_h (nm)	[CTAB]	D_h (nm)
0.004	3.5	0.010	3.4	0.01	3.7	0.03	3.9
0.008	3.6	0.020	3.7	0.02	3.7	0.05	4.2
0.010	3.8	0.025	3.9	0.03	4.0	0.10	5.9
0.020	6.0	0.030	4.5	0.05	4.9	0.15	8.0
0.030	9.4	0.035	6.8	0.06	8.2	0.20	10.2
0.040	15.8	0.040	10.3	0.07	15.1	0.25	13.5
0.050	23.8	0.050	18.1	0.08	18.3	0.30	18.6
	turbid		turbid	0.10	32.8 turbid		turbid

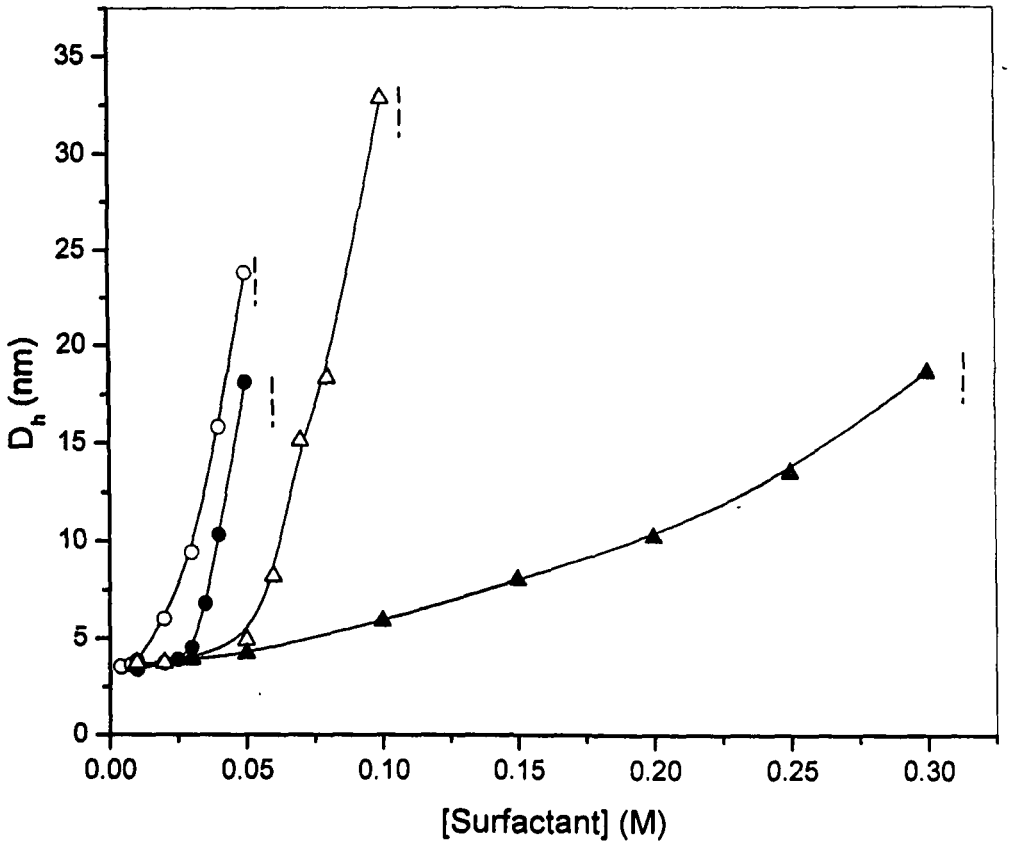


Fig. 4.1(b). Variation of hydrodynamic diameter (D_h) with the [surfactant] at 30 °C (upto the solubility limit indicated by dotted lines): 16–4–16 (○); 16–5–16 (●); 16–6–16 (Δ); CTAB (▲).

Table 4.2 (a): Effect of addition of KBr on the relative viscosity (η_r) of 0.03 M surfactant solutions at 30 °C.

16-4-16		16-5-16		16-6-16		CTAB	
[KBr] (M)	η_r	[KBr] (M)	η_r	[KBr] (M)	η_r	[KBr] (M)	η_r
0	1.74	0	1.30	0	1.27	0	1.09
0.0005	1.99	0.001	1.40	0.001	1.32	0.001	1.10
0.0010	2.42	0.005	1.56	0.005	1.34	0.005	1.10
0.0013	3.33	0.010	5.24	0.010	1.53	0.010	1.13
0.0020	5.15	0.020	28.44	0.020	2.03	0.020	1.16
0.0030	8.82	0.030	89.99	0.030	2.61	0.030	1.19
0.0040	12.22						
0.0050	17.19						
0.0075	23.72						

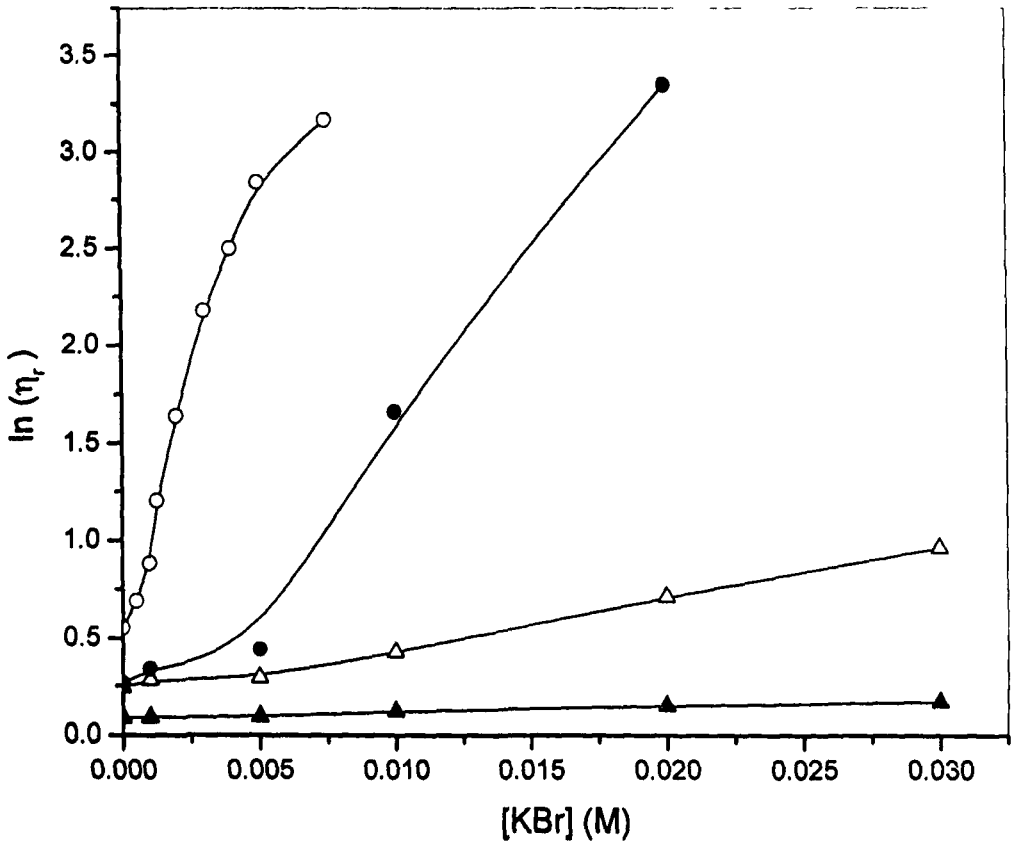


Fig. 4.2(a). Variation of ln (η_r) with the added [KBr] to 0.03 M surfactant solutions at 30 °C: 16–4–16 (○); 16–5–16 (●); 16–6–16 (Δ); CTAB (▲).

Table 4.2 (b): Effect of addition of KBr on the hydrodynamic diameter (D_h) of 0.03 M surfactant solutions at 30 °C.

16-4-16		16-5-16		16-6-16		CTAB	
[KBr] (M)	D_h (nm)	[KBr] (M)	D_h (nm)	[KBr] (M)	D_h (nm)	[KBr] (M)	D_h (nm)
0	9.4	0	4.5	0	4.0	0	4.1
0.0010	11.2	0.001	4.6	0.001	4.4	0.001	4.1
0.0015	18.2	0.002	4.7	0.002	4.5	0.002	4.2
0.0020	26.0	0.005	5.9	0.005	4.9	0.005	4.9
0.0030	32.1	0.010	14.0	0.010	6.8	0.010	5.5
0.0050	35.2	0.020	28.8	0.020	9.8	0.020	6.3
		0.030	39.7	0.030	15.2	0.030	7.1

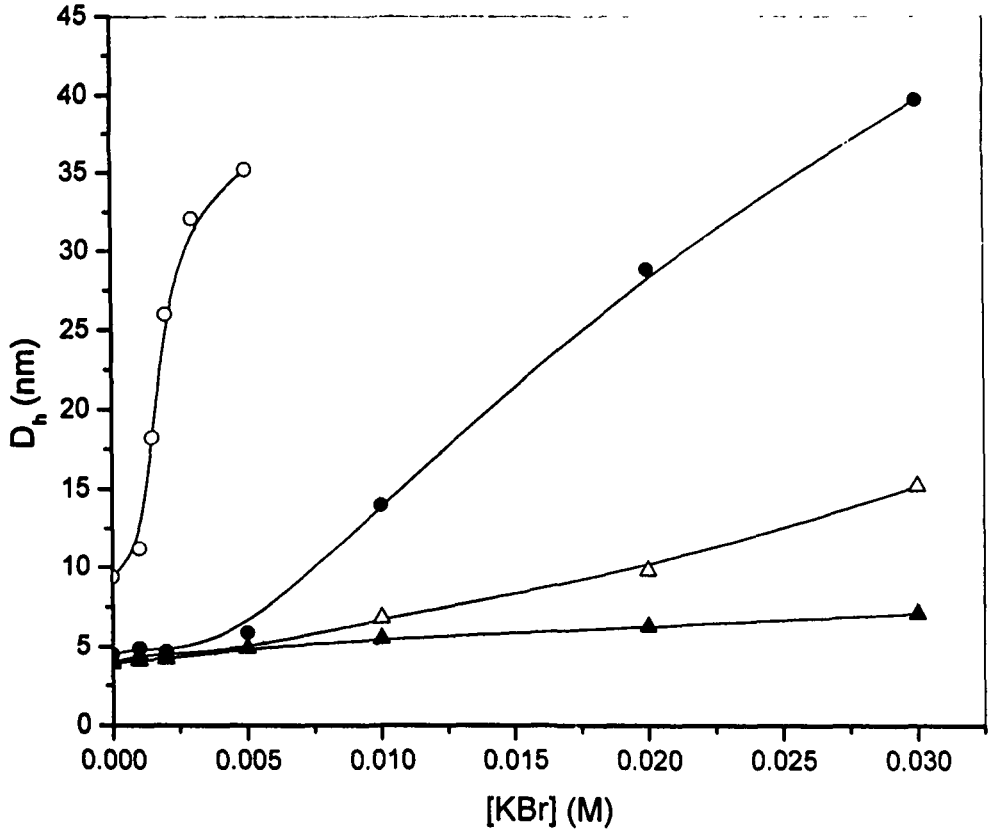


Fig. 4.2(b). Variation of hydrodynamic diameter (D_h) with the added [KBr] to 0.03 M surfactant solutions at 30 °C: 16–4–16 (○); 16–5–16 (●); 16–6–16 (Δ); CTAB (▲).

Table 4.3 (a): Effect of the addition of alcohols on the relative viscosity (η_r) of 0.03 M 16-4-16 solutions at 30 °C.

[C_4OH] (M)	η_r	[C_5OH] (M)	η_r	[C_6OH] (M)	η_r
0	1.74	0	1.74	0	1.74
0.024	2.05	0.010	2.03	0.0040	2.75
0.040	2.37	0.015	2.60	0.0080	3.97
0.060	2.87	0.020	2.72	0.0120	5.75
0.080	3.10	0.025	3.11	0.0160	7.10
0.100	3.42	0.030	3.55	0.0195	9.49
0.120	4.07	0.035	4.62	0.0234	15.33
0.135	4.78	0.040	5.91	0.0260	21.76
0.150	5.45	0.044	8.42	0.0300	35.50
0.166	6.28	0.049	10.80	0.0366	68.03
	turbid	0.054	13.02		turbid
		0.061	17.36		
			turbid		

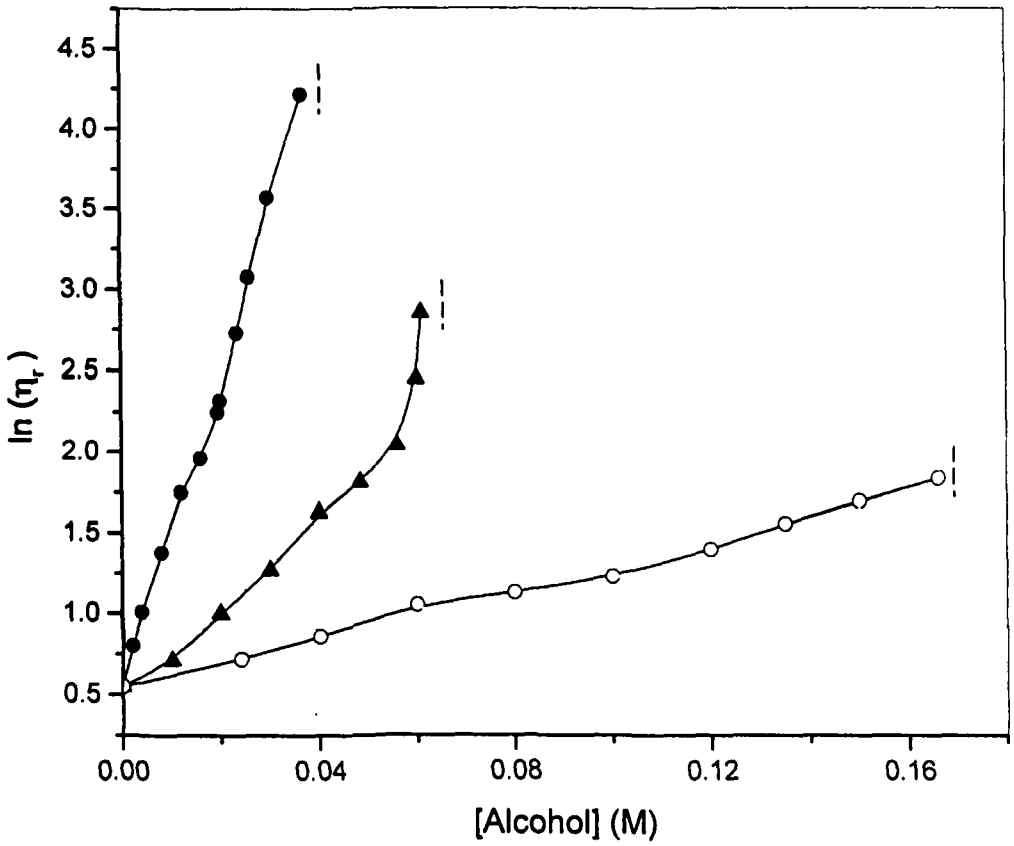


Fig. 4.3(a). Variation of ln (η_r) with the added [alcohol] to 0.03 M 16–4–16 solutions at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.3 (b): Effect of the addition of alcohols on the hydrodynamic diameter (D_h) of 0.03 M 16-4-16 solutions at 30 °C.

[C_4OH] (M)	D_h (nm)	[C_5OH] (M)	D_h (nm)	[C_6OH] (M)	D_h (nm)
0	9.4	0	9.4	0	9.4
0.02	9.5	0.010	11.5	0.004	12.8
0.04	9.6	0.020	11.6	0.008	15.9
0.06	12.6	0.030	13.8	0.012	18.1
0.08	15.4	0.040	16.5	0.015	22.5
0.10	21.0	0.050	21.6	0.020	32.1
0.12	26.1	0.055	26.4	0.023	36.2
0.15	36.7	0.060	32.7	0.025	37.7
	turbid		turbid	0.030	45.3
				0.040	50.9
					turbid

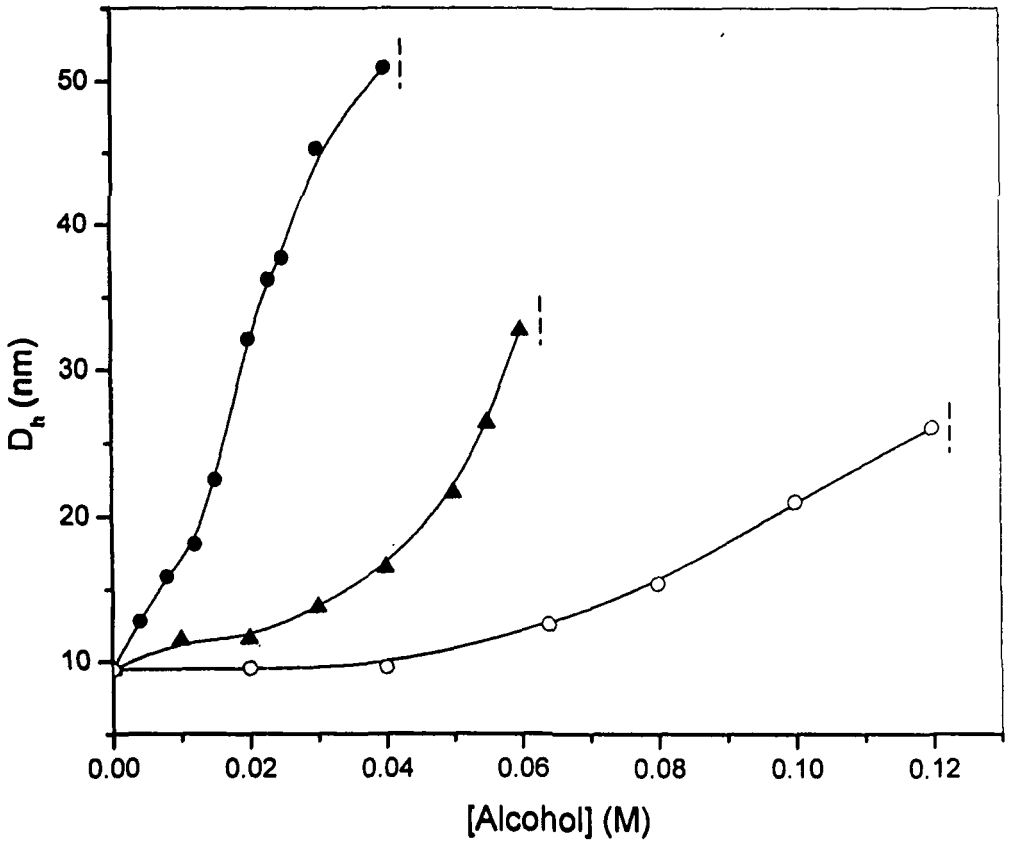


Fig.4.3(b). Variation of hydrodynamic diameter (D_h) with the added [alcohol] to 0.03 M 16–4–16 solutions at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.4 (a): Effect of the addition of alcohols on the relative viscosity (η_r) of 0.03 M 16-5-16 solutions at 30 °C.

$[C_4OH]$ (M)	η_r	$[C_5OH]$ (M)	η_r	$[C_6OH]$ (M)	η_r
0	1.30	0	1.30	0	1.30
0.020	1.36	0.050	1.32	0.005	1.32
0.040	1.39	0.010	1.38	0.010	1.63
0.060	1.46	0.015	1.45	0.015	1.93
0.080	1.50	0.020	1.55	0.020	2.06
0.100	1.70	0.025	1.58	0.023	2.52
0.120	1.85	0.030	1.80	0.025	2.62
0.136	1.89	0.040	2.05	0.028	3.03
0.150	2.12	0.050	2.58	0.030	3.60
0.155	2.26	0.058	3.13	0.035	6.20
0.160	2.36	0.064	3.63	0.040	9.90
0.165	2.54		turbid	0.045	17.65
0.177	2.90 turbid				turbid

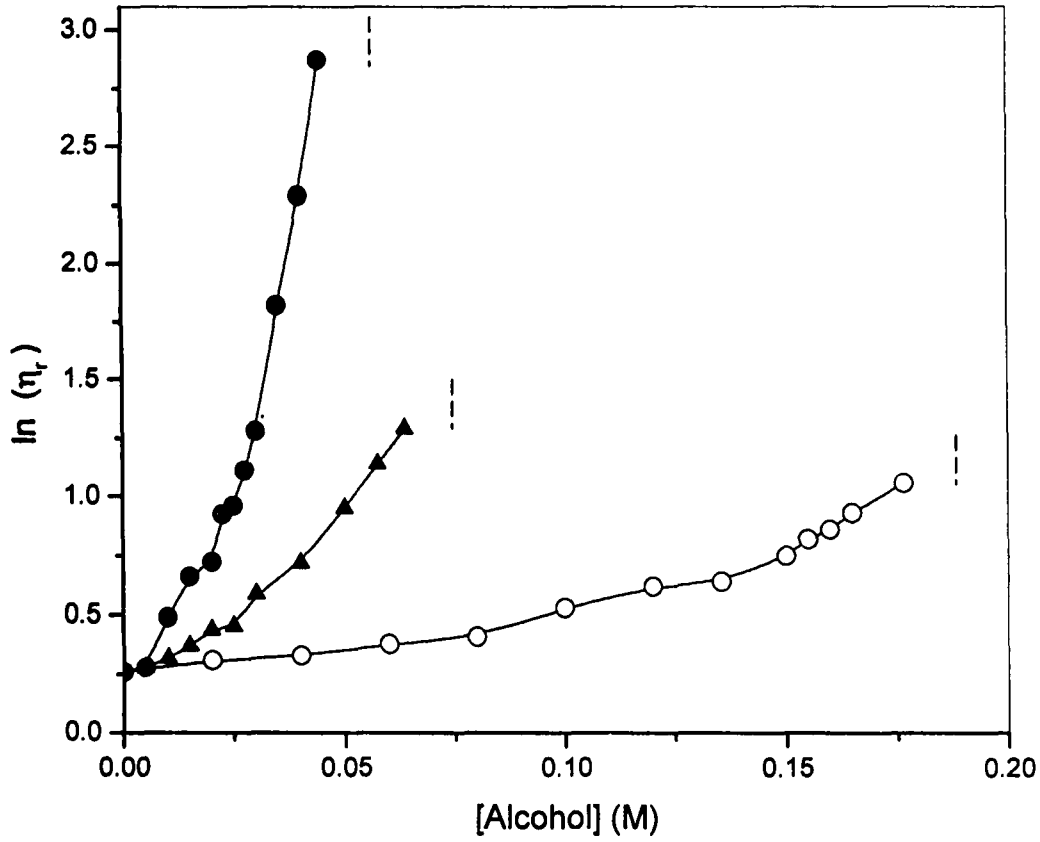


Fig. 4.4(a). Variation of ln (η_r) with the added [alcohol] to 0.03 M 16–5–16 solutions at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.4 (b): Effect of the addition of alcohols on the hydrodynamic diameter (D_h) of 0.03 M 16-5-16 solutions at 30 °C.

[C_4OH] (M)	D_h (nm)	[C_5OH] (M)	D_h (nm)	[C_6OH] (M)	D_h (nm)
0	4.5	0	4.5	0	4.5
0.020	4.5	0.010	4.5	0.010	4.6
0.040	4.5	0.015	4.5	0.020	5.2
0.060	4.5	0.020	4.6	0.023	6.0
0.080	4.5	0.025	4.7	0.025	7.3
0.100	4.9	0.030	5.4	0.030	11.3
0.120	5.5	0.040	7.6	0.035	17.6
0.130	5.9	0.050	11.6	0.040	25.9
0.140	6.1	0.055	15.3	0.045	28.9
0.150	7.3	0.060	18.1		turbid
0.155	7.8		turbid		
0.160	8.3				
0.165	9.0				
0.177	10.7				
	turbid				

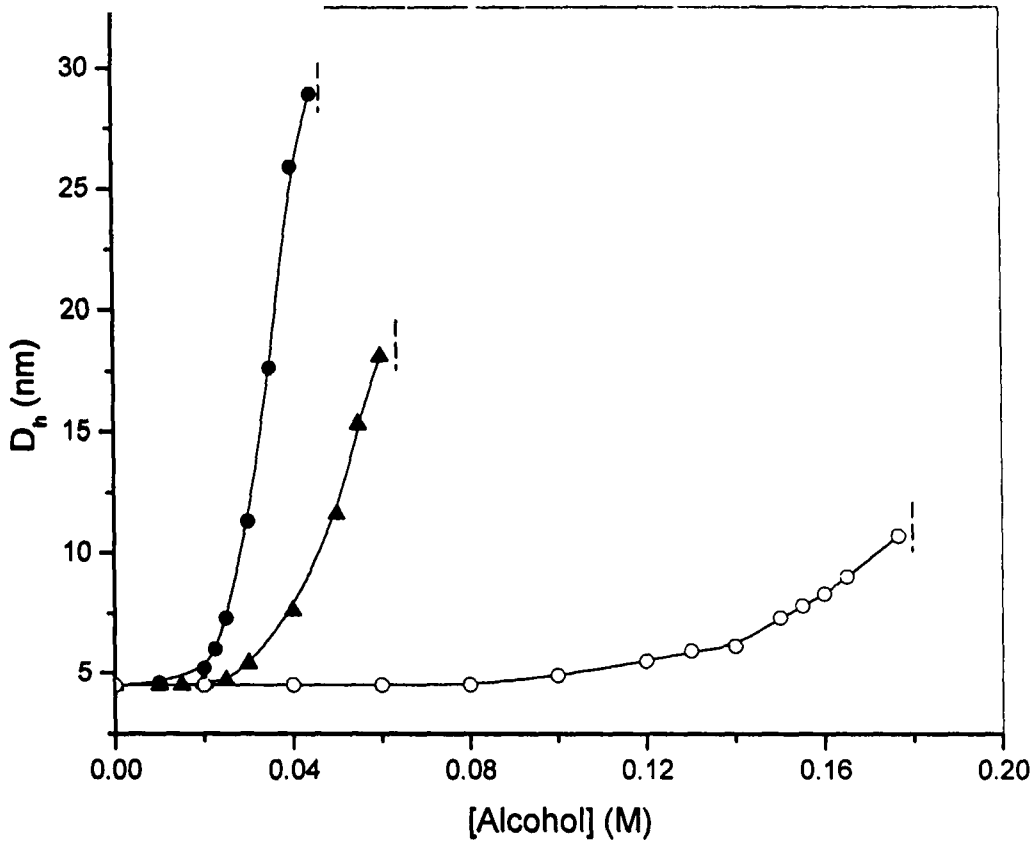


Fig.4.4(b). Variation of hydrodynamic diameter (D_h) with the added [alcohol] to 0.03 M 16–5–16 solutions at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH

Table 4.5 (a): Effect of the addition of alcohols on the relative viscosity (η_r) *of 0.03 M 16-6-16 solutions at 30 °C.*

$[C_4OH]$ (M)	η_r	$[C_5OH]$ (M)	η_r	$[C_6OH]$ (M)	η_r
0	1.27	0	1.27	0	1.27
0.020	1.29	0.010	1.28	0.004	1.36
0.040	1.30	0.020	1.31	0.008	1.42
0.060	1.31	0.025	1.32	0.010	1.48
0.080	1.31	0.030	1.34	0.014	1.52
0.106	1.33	0.035	1.35	0.018	1.62
0.127	1.35	0.040	1.37	0.020	1.68
0.140	1.39	0.043	1.43	0.022	1.72
0.150	1.44	0.045	1.44	0.026	1.75
0.156	1.55	0.050	1.49	0.030	1.86
	turbid	0.055	1.53	0.032	1.92
		0.061	1.57	0.034	2.02
			turbid	0.036	2.24
				0.038	2.44
				0.040	2.79
				0.042	4.12
					turbid

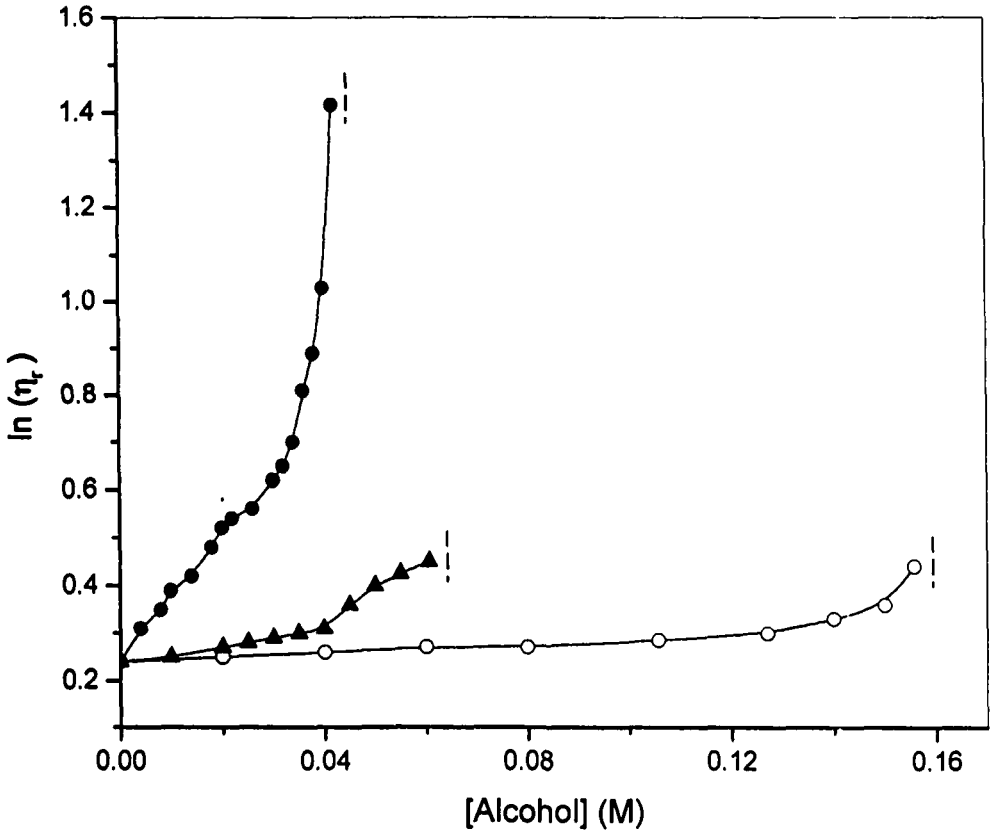


Fig.4.5(a). Variation of ln (η_r) with the added [alcohol] to 0.03 M 16–6–16 solutions at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.5 (b): Effect of the addition of alcohols on the hydrodynamic diameter (D_h) of 0.03 M 16-6-16 solutions at 30 °C.

[C_4OH] (M)	D_h (nm)	[C_5OH] (M)	D_h (nm)	[C_6OH] (M)	D_h (nm)
0	4.0	0	4.0	0	4.0
0.020	4.0	0.010	4.2	0.005	4.0
0.040	4.0	0.020	4.3	0.010	4.1
0.060	4.0	0.030	4.9	0.015	4.8
0.080	4.1	0.040	6.3	0.020	5.0
0.100	4.2	0.050	7.8	0.026	6.5
0.130	4.8	0.055	8.3	0.030	8.6
0.140	5.0	0.060	9.3	0.034	10.4
0.150	5.6		turbid	0.036	12.1
0.155	5.9			0.038	14.0
	turbid			0.040	17.0
					turbid

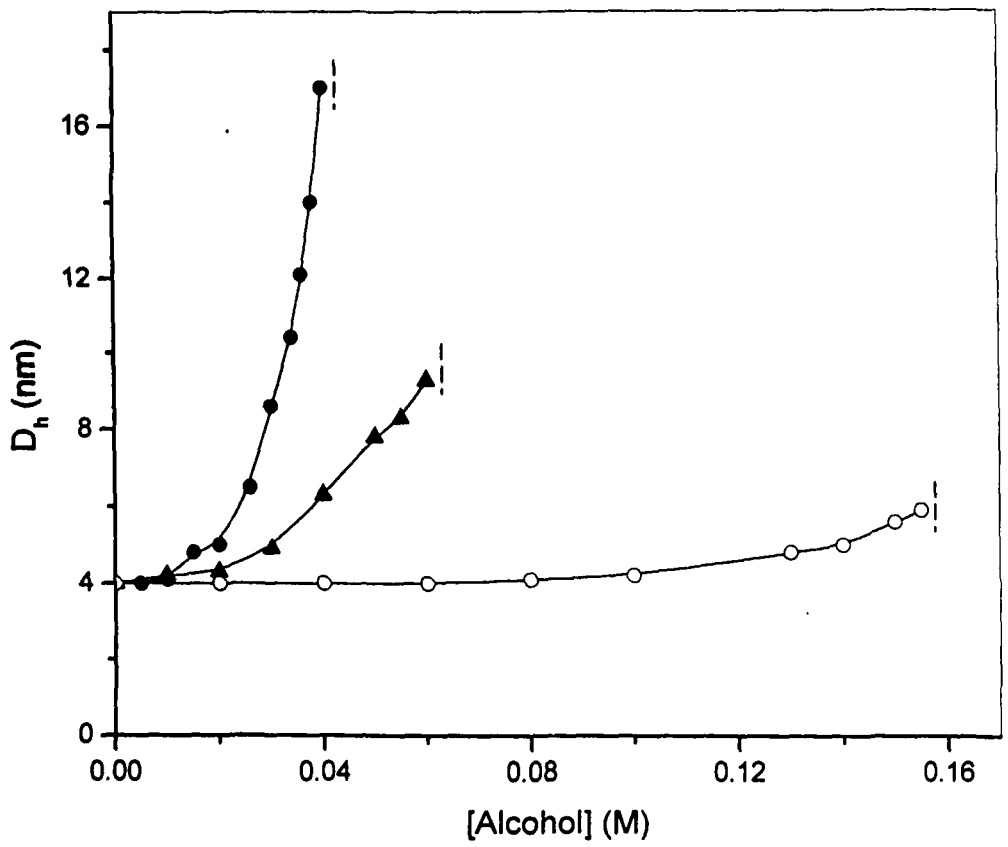


Fig.4.5(b). Variation of hydrodynamic diameter (D_h) with the added [alcohol] to 0.03 M 16–6–16 solutions at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.6 (a): Effect of addition of alcohols on the relative viscosity (η_r) of 0.03 M 16-4-16 + 0.001 M KBr solutions at 30 °C.

$[C_4OH]$ (M)	η_r	$[C_5OH]$ (M)	η_r	$[C_6OH]$ (M)	η_r
0	2.42	0	2.42	0	2.42
0.020	3.77	0.005	6.22	0.0025	5.19
0.040	6.35	0.010	8.20	0.0050	11.51
0.060	7.02	0.015	11.01	0.0080	14.06
0.080	7.42	0.020	14.92	0.0090	37.03
0.090	7.79	0.025	23.20	0.0100	57.50
0.100	9.83	0.030	32.18	0.0120	95.02
0.110	12.59	0.040	49.10	0.0150	228.23
0.120	17.61	0.050	86.77	0.0160	355.14
0.130	20.43	0.060	104.13		turbid
0.140	24.42		turbid		
0.150	26.40				
0.160	30.08				
	turbid				

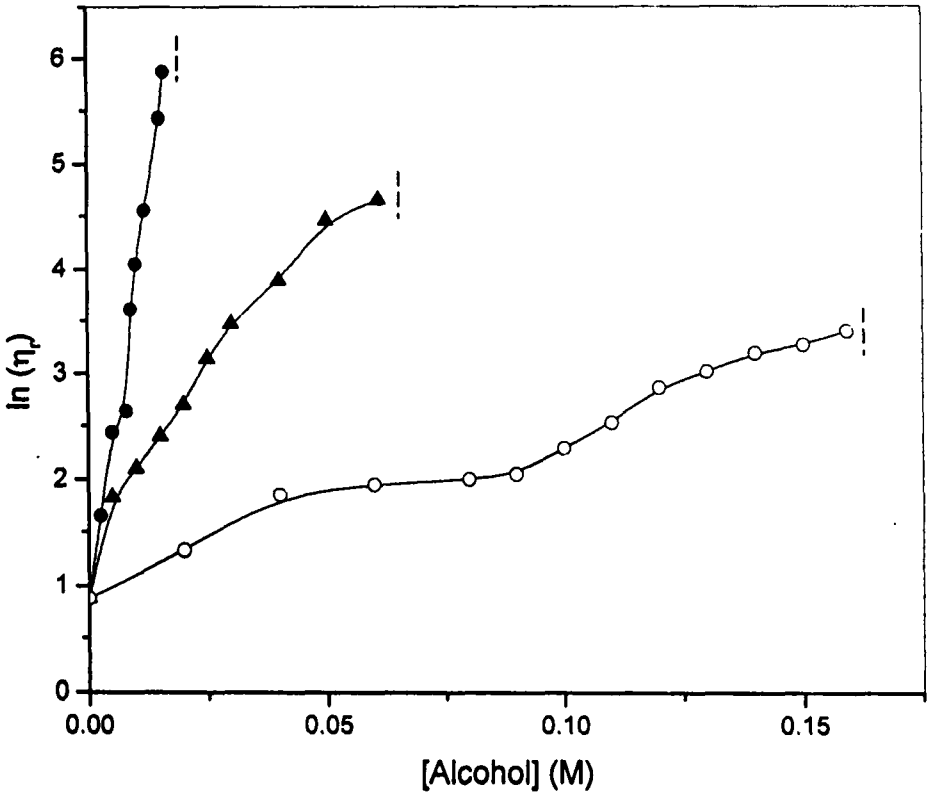


Fig. 4.6(a). Variation of ln (η_r) with the added [alcohol] to 0.03 M 16–4–16 solutions in the presence of 0.001 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.6 (b): Effect of addition of alcohols on the hydrodynamic diameter (D_h) of 0.03 M 16-4-16 + 0.001 M KBr solutions at 30 °C.

[C_4OH] (M)	D_h (nm)	[C_5OH] (M)	D_h (nm)	[C_6OH] (M)	D_h (nm)
0	11.2	0	11.2	0	11.2
0.02	11.7	0.005	11.3	0.0025	14.8
0.04	16.3	0.010	15.7	0.0050	19.4
0.06	20.2	0.015	19.7	0.0080	32.3
0.09	25.7	0.020	20.3	0.0090	34.0
0.10	26.7	0.030	25.3	0.0100	38.1
0.12	29.8	0.040	27.5	0.0120	41.3
0.15	37.6	0.050	28.6	0.0150	45.9
	turbid		turbid		turbid

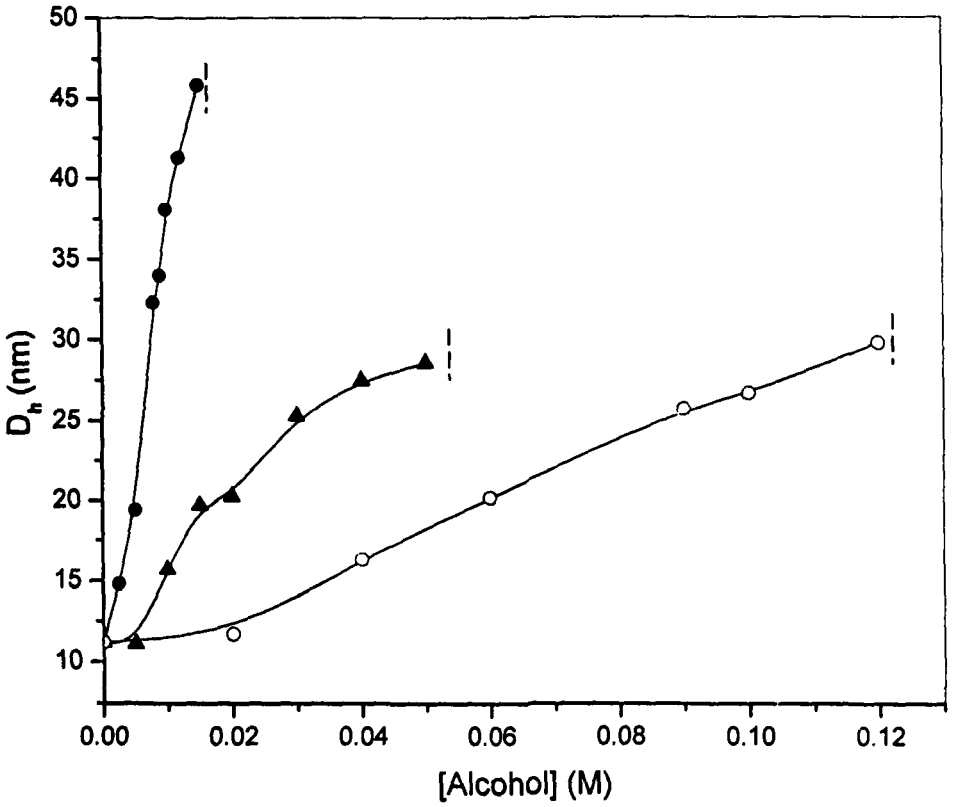


Fig. 4.6(b). Variation of hydrodynamic diameter (D_h) with the added [alcohol] to 0.03 M 16–4–16 solutions in the presence of 0.001 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.7 (a): Effect of addition of alcohols on the relative viscosity (η_r) of 0.03 M 16-5-16 + 0.005 M KBr solutions at 30 °C.

$[C_4OH]$ (M)	η_r	$[C_5OH]$ (M)	η_r	$[C_6OH]$ (M)	η_r
0	1.56	0	1.56	0	1.56
0.01	1.94	0.005	2.01	0.0015	1.58
0.02	2.09	0.010	2.52	0.0030	2.06
0.03	2.37	0.015	3.50	0.0040	2.24
0.04	2.40	0.020	4.67	0.0050	2.66
0.05	2.81	0.025	4.87	0.0070	3.50
0.06	3.09	0.030	9.66	0.0080	4.20
0.07	3.50	0.035	16.24	0.0100	5.30
0.08	3.70	0.040	25.20	0.0120	6.90
0.09	4.01	0.045	35.01	0.0130	9.83
0.10	4.28	0.050	48.02	0.0150	17.69
0.11	5.30		turbid	0.0170	40.50
0.12	6.23			0.0200	72.31
0.13	7.32			0.0240	364.44
0.14	8.40				turbid
0.15	9.53				
0.16	10.30				
0.17	12.15				
	turbid				

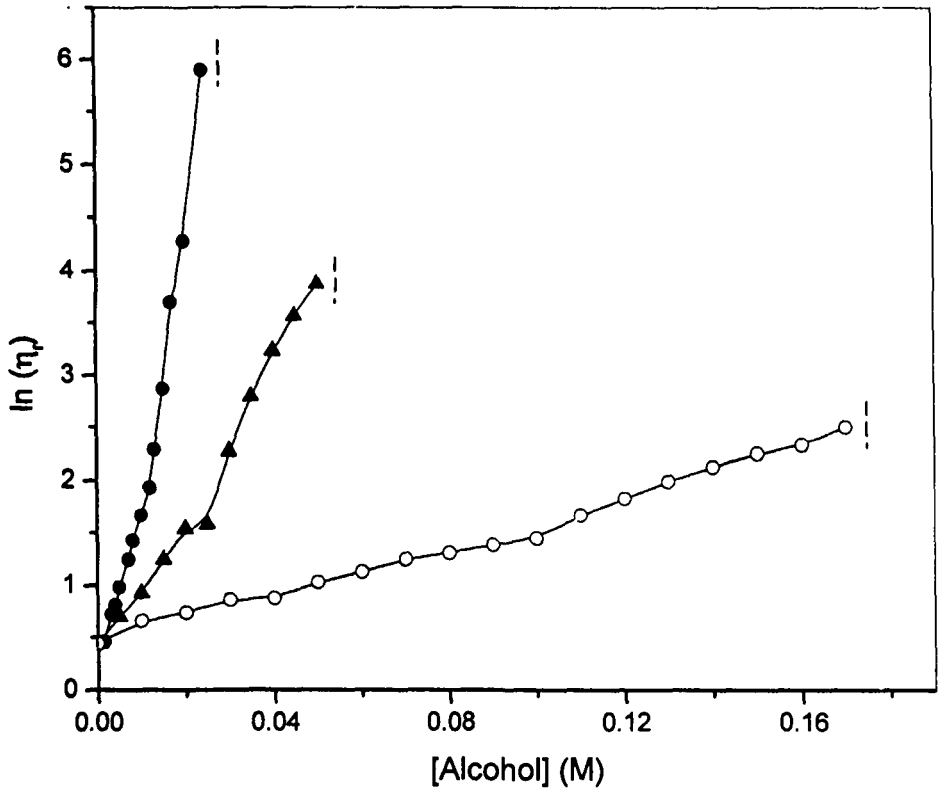


Fig. 4.7(a). Variation of ln (η_r) with the added [alcohol] to 0.03 M 16–5–16 solutions in the presence of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.7 (b): Effect of addition of alcohols on the hydrodynamic diameter (D_h) of 0.03 M 16-5-16 + 0.005 M KBr solutions at 30 °C.

$[C_4OH]$ (M)	D_h (nm)	$[C_5OH]$ (M)	D_h (nm)	$[C_6OH]$ (M)	D_h (nm)
0	5.9	0	5.9	0	5.9
0.01	5.9	0.005	5.9	0.002	5.9
0.02	5.9	0.010	5.9	0.005	5.9
0.04	5.9	0.015	5.9	0.008	6.3
0.06	5.9	0.020	5.9	0.012	7.2
0.08	7.0	0.025	7.1	0.013	8.3
0.10	8.1	0.030	8.3	0.015	9.1
0.12	9.3	0.035	10.8	0.017	10.8
0.13	10.0	0.040	15.3	0.020	24.9
0.15	11.5	0.045	20.7	0.024	34.4
0.17	13.1	0.050	23.9		turbid
	turbid		turbid		

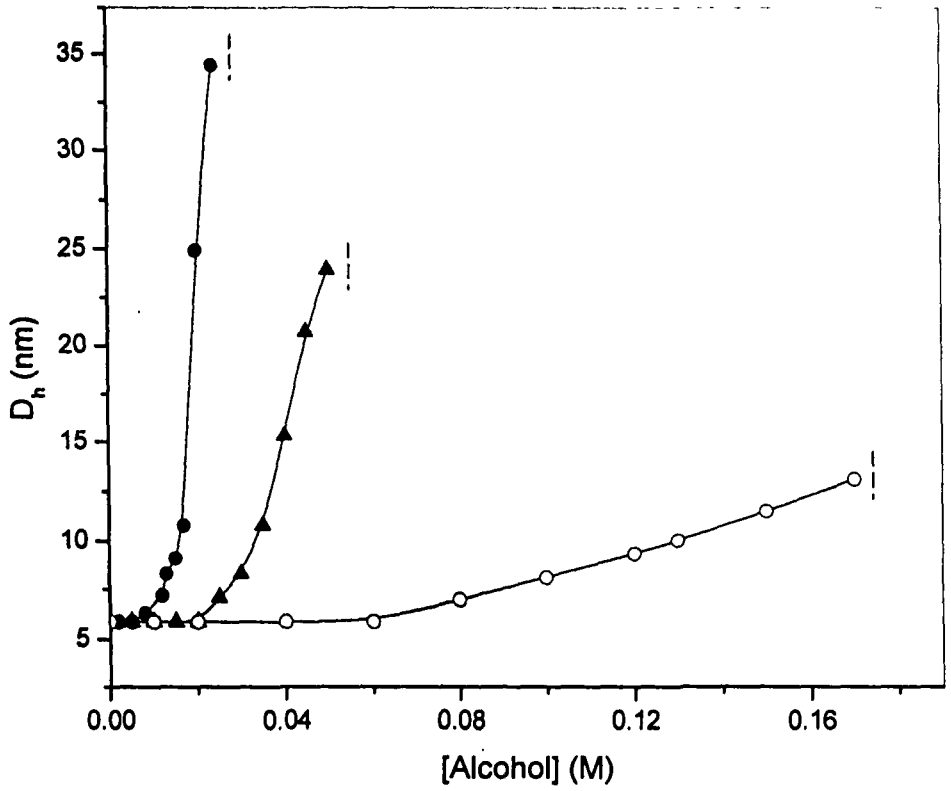


Fig. 4.7(b). Variation of hydrodynamic diameter (D_h) with the added [alcohol] to 0.03 M 16–5–16 solutions in the presence of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.8 (a): Effect of addition of alcohols on the relative viscosity (η_r) of 0.03 M 16-6-16 + 0.005 M KBr solutions at 30 °C.

$[C_4OH]$ (M)	η_r	$[C_5OH]$ (M)	η_r	$[C_6OH]$ (M)	η_r
0	1.34	0	1.34	0	1.34
0.020	1.38	0.010	1.45	0.010	1.68
0.040	1.40	0.020	1.50	0.020	2.01
0.060	1.46	0.030	1.55	0.030	3.41
0.080	1.50	0.040	1.65	0.035	6.73
0.101	1.56	0.055	1.80	0.040	11.86
0.117	1.64	0.065	2.20	0.045	23.62
0.131	1.68	0.072	3.05	0.049	56.20
0.145	1.88	0.080	3.54	0.052	95.80
0.160	2.24	0.090	5.76		turbid
0.170	2.68		turbid		
0.180	2.98				
	turbid				

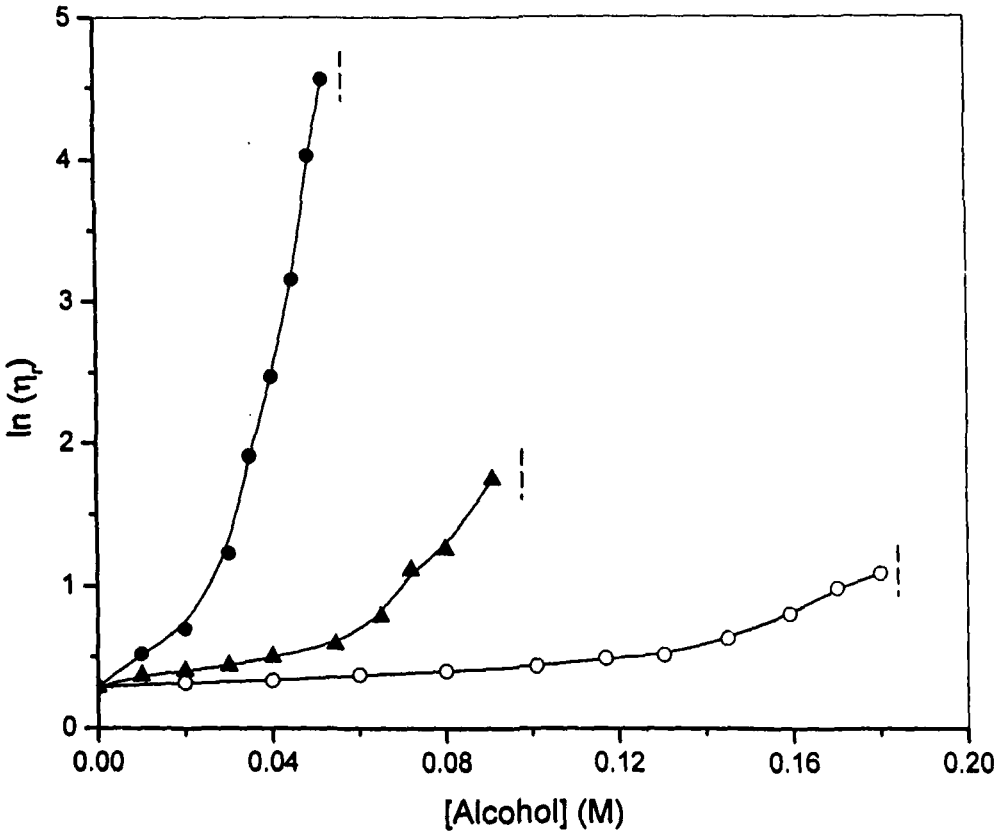


Fig. 4.8(a). Variation of ln (η_r) with the added [alcohol] to 0.03 M 16–6–16 solutions in the presence of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.8 (b): Effect of addition of alcohols on the hydrodynamic diameter (D_h) of 0.03 M 16-6-16 + 0.005 M KBr solutions at 30 °C.

[C_4OH] (M)	D_h (nm)	[C_5OH] (M)	D_h (nm)	[C_6OH] (M)	D_h (nm)
0	4.9	0	4.9	0	4.9
0.02	5.0	0.010	5.1	0.010	5.4
0.04	5.1	0.020	5.6	0.020	7.4
0.06	5.2	0.030	6.3	0.030	12.0
0.08	5.4	0.040	7.1	0.035	16.6
0.10	5.5	0.055	9.1	0.040	19.5
0.11	5.6	0.060	10.4	0.045	24.3
0.13	5.8	0.065	11.6	0.049	26.3
0.14	6.5	0.070	12.5	0.052	27.9
0.15	7.1	0.075	14.6		turbid
0.16	8.5	0.080	17.6		
0.17	9.6	0.090	20.7		
0.18	11.5		turbid		
	turbid				

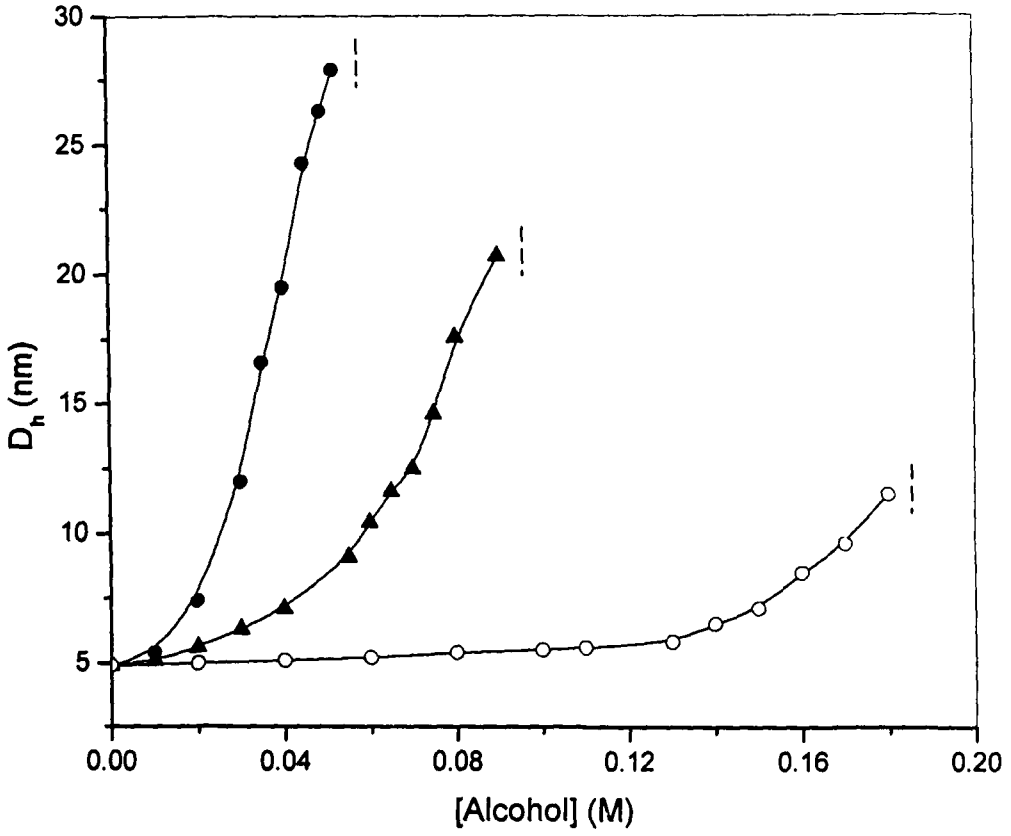


Fig. 4.8(b). Variation of hydrodynamic diameter (D_h) with the added [alcohol] to 0.03 M 16–6–16 solutions in the presence of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_4OH (○); C_5OH (▲); C_6OH (●).

Table 4.9 (a): Effect of addition of hexylamine on the relative viscosity (η_r) of 0.03 M surfactants solutions at 30 °C.

16-4-16		16-5-16		16-6-16	
$[C_6NH_2]$ (M)	η_r	$[C_6NH_2]$ (M)	η_r	$[C_6NH_2]$ (M)	η_r
0	1.74	0	1.30	0	1.70
0.002	2.69	0.005	1.30	0.0060	1.28
0.004	3.22	0.010	1.67	0.0100	1.30
0.006	4.99	0.015	1.82	0.0150	1.31
0.008	5.88	0.020	1.86	0.0200	1.32
0.010	9.22	0.025	1.98	0.0250	1.46
0.012	10.81	0.030	2.06	0.0290	1.62
0.014	12.62	0.035	2.41	0.0350	1.68
0.015	14.79	0.039	2.89	0.0390	1.86
0.020	22.56	0.051	3.12	0.0430	2.12
0.025	15.18	0.059	2.94	0.0460	2.42
0.029	7.910		turbid	0.0463	2.82
	turbid			0.0491	3.26
					turbid

Table 4.10 (a): Effect of addition of hexylamine on the viscosity (η_r) of 0.03 M surfactants + 0.001M / 0.005 M KBr at 30 °C.

16-4-16		16-5-16		16-6-16	
$[C_6NH_2]$ (M)	η_r	$[C_6NH_2]$ (M)	η_r	$[C_6NH_2]$ (M)	η_r
0	2.42	0	1.56	0	1.34
0.0010	4.98	0.0050	2.40	0.005	1.35
0.0020	5.54	0.0100	3.01	0.010	1.36
0.0050	7.52	0.0150	3.72	0.015	1.41
0.0080	10.11	0.0200	3.95	0.020	1.43
0.0100	13.21	0.0225	4.21	0.025	1.60
0.0120	16.53	0.0238	4.92	0.030	1.94
0.0150	20.34	0.0250	6.57	0.035	2.56
0.0176	21.20	0.0300	8.31	0.038	3.13
0.0200	29.53	0.0393	6.77	0.040	3.91
0.0220	32.02		turbid	0.043	4.30
0.0245	43.39			0.044	4.73
	turbid				turbid

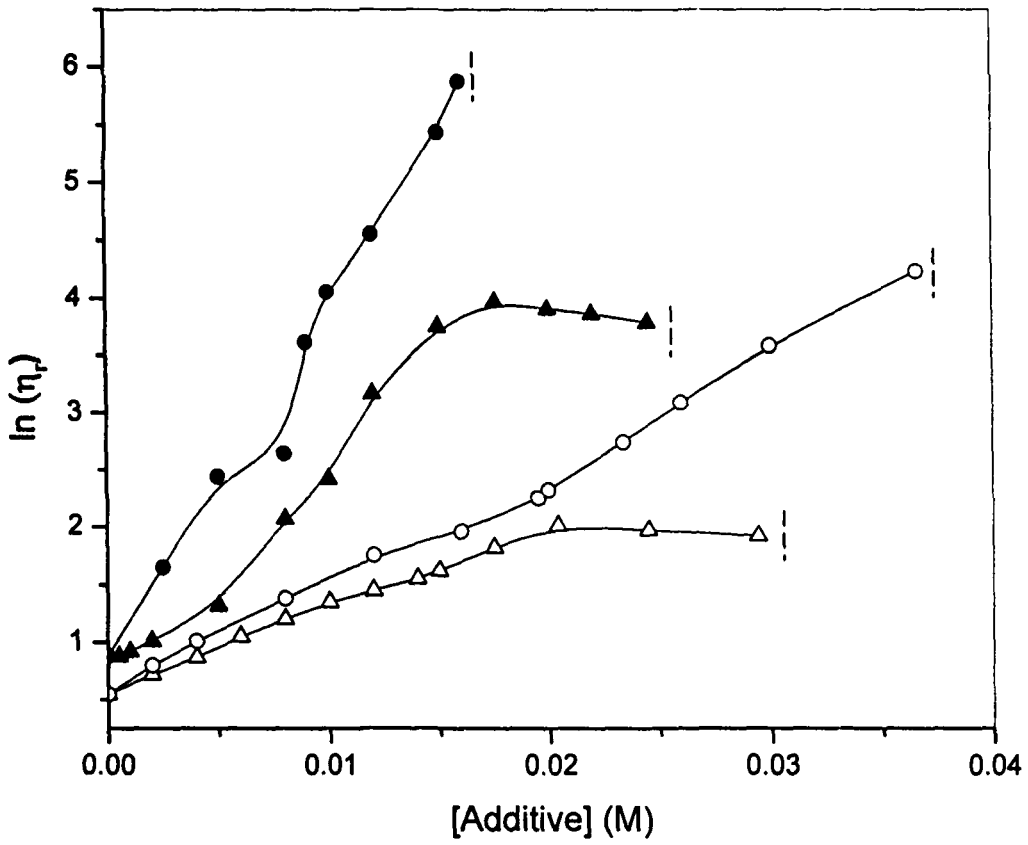


Fig. 4.9(a). Variation of ln (η_r) with [additive] (of equal chain length) to 0.03 M 16–4–16 solutions in the presence (filled symbols) and absence (open symbols) of 0.001 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_6OH (●,○); C_6NH_2 (▲,Δ).

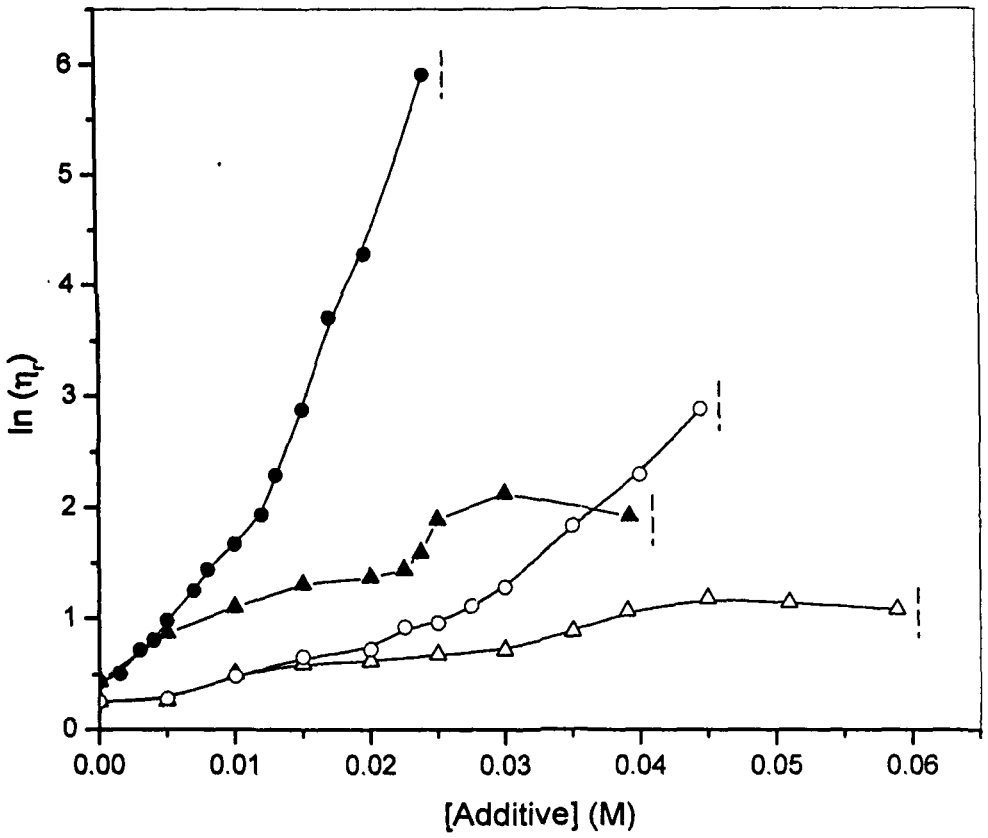


Fig.4.10(a). Variation of ln (η_r) with [additive] (of equal chain length) to 0.03 M 16–5–16 solutions in the presence (filled symbols) and absence (open symbols) of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_6OH (●,○); C_6NH_2 (▲,Δ).

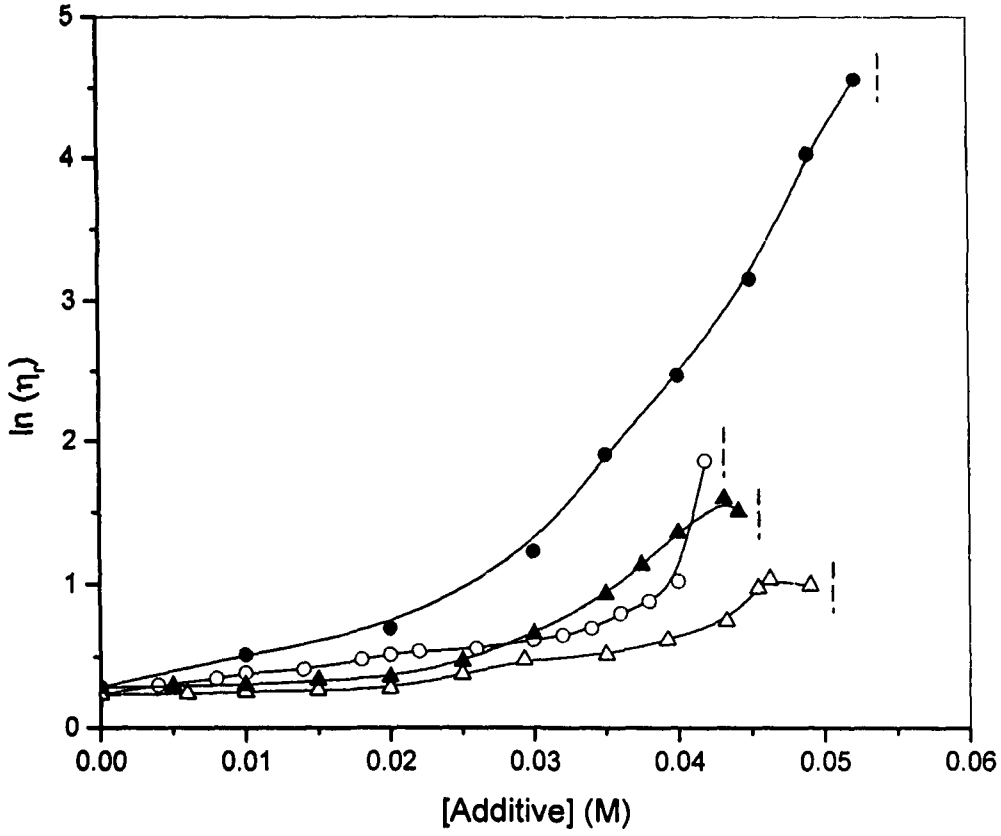


Fig. 4.11(a). Variation of ln (η_r) with [additive] (of equal chain length) to 0.03 M 16–6–16 solutions in the presence (filled symbols) and absence (open symbols) of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_6OH (●,○); C_6NH_2 (▲,Δ).

Table 4.9 (b): Effect of addition of hexylamine on the hydrodynamic diameter (D_h) of 0.03 M surfactants at 30 °C.

16-4-16		16-5-16		16-6-16	
$[C_6NH_2]$ (M)	D_h (nm)	$[C_6NH_2]$ (M)	D_h (nm)	$[C_6NH_2]$ (M)	D_h (nm)
0	9.40	0	4.5	0	4.0
0.005	9.50	0.005	4.6	0.005	4.0
0.008	9.55	0.010	4.7	0.010	4.0
0.010	11.80	0.015	4.7	0.015	4.2
0.015	13.20	0.020	5.0	0.020	4.3
0.020	14.20	0.025	5.3	0.025	4.5
0.025	12.10	0.030	5.6	0.030	4.8
	turbid	0.035	6.4	0.035	5.1
		0.040	8.3	0.040	6.5
		0.045	9.2	0.043	7.4
		0.050	9.3	0.045	8.6
		0.059	8.5	0.047	9.9
			turbid	0.049	9.8
					turbid

Table 4.10 (b): Effect of addition of hexylamine on the hydrodynamic diameter (D_h) of 0.03 M surfactants + 0.001M / 0.005 M KBr at 30 °C.

16-4-16		16-5-16		16-6-16	
$[C_6NH_2]$ (M)	D_h (nm)	$[C_6NH_2]$ (M)	D_h (nm)	$[C_6NH_2]$ (M)	D_h (nm)
0.0	11.2	0	5.9	0	4.9
0.005	15.5	0.005	5.9	0.005	4.9
0.008	21.3	0.010	5.9	0.010	4.9
0.010	25.5	0.015	7.0	0.015	4.9
0.015	35.6	0.020	10.3	0.020	5.0
0.020	37.2	0.023	15.7	0.025	7.2
0.025	34.8	0.025	18.3	0.030	9.7
	turbid	0.030	19.6	0.035	12.0
		0.039	18.2	0.038	14.5
			turbid	0.040	15.5
				0.044	15.3
					turbid

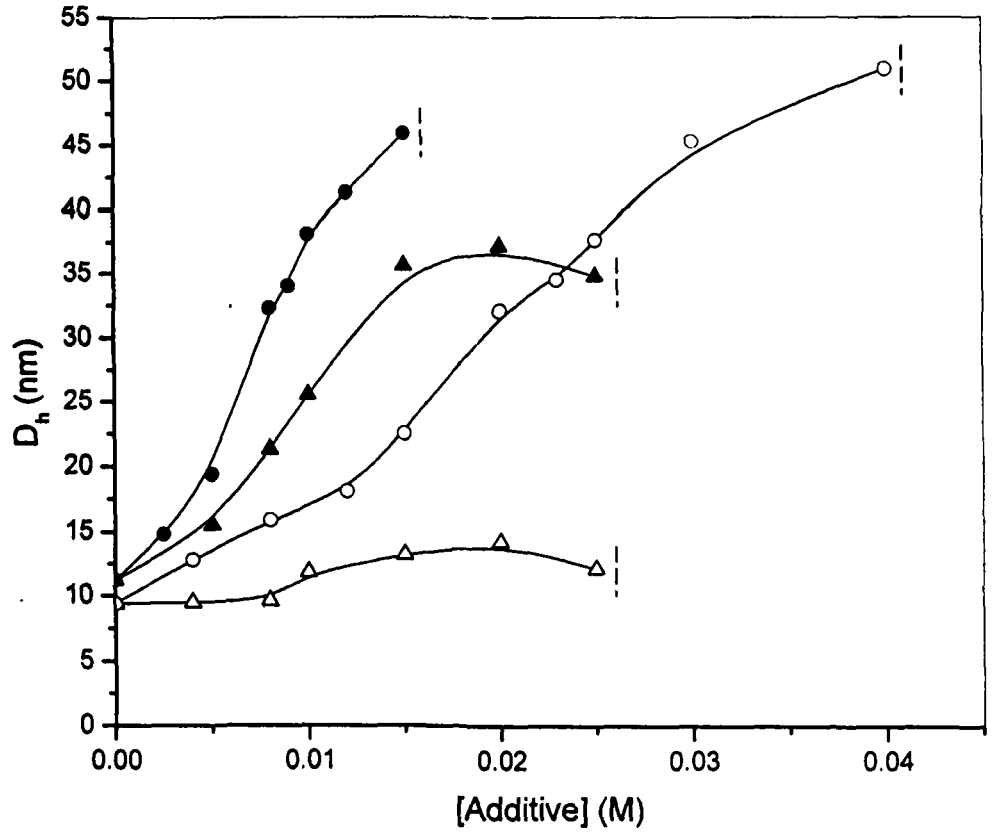


Fig.4.9(b). Variation of hydrodynamic diameter (D_h) with [additive] (of equal chain length) to 0.03 M 16–4–16 solutions in the presence (filled symbols) and absence (open symbols) of 0.001 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_6OH (●,○); C_6NH_2 (▲,Δ).

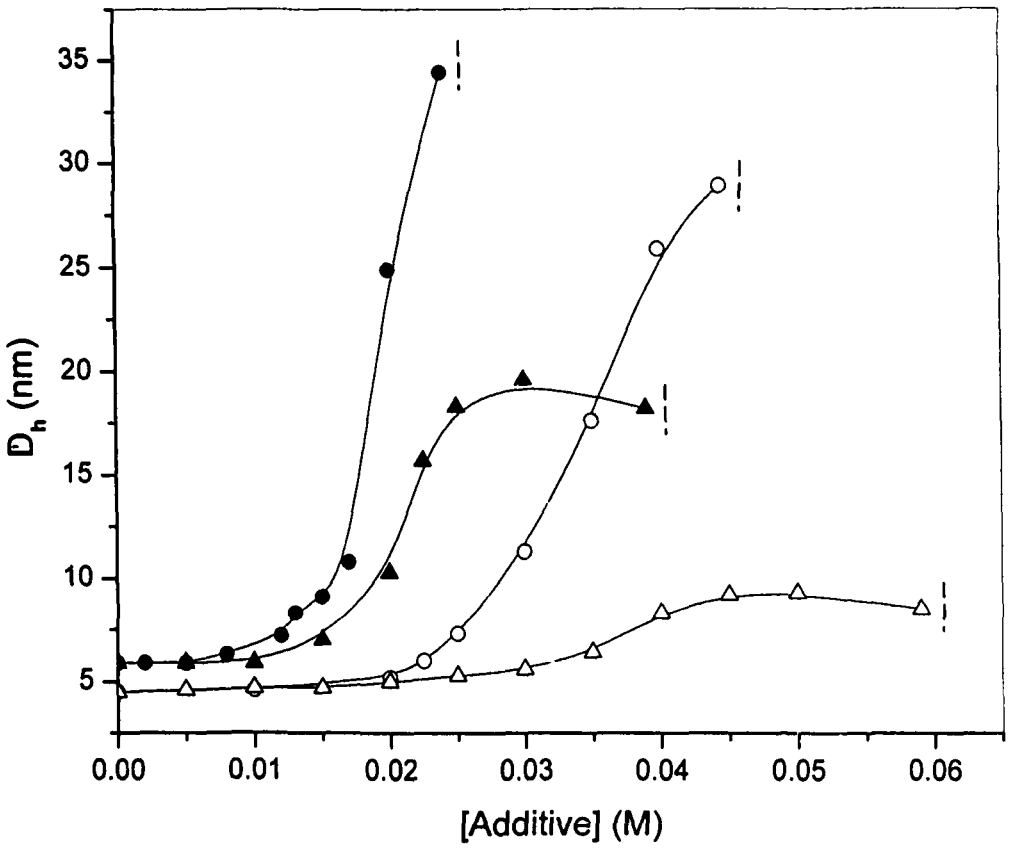


Fig. 4.10(b). Variation of hydrodynamic diameter (D_h) with [additive] (of equal chain length) to 0.03 M 16–5–16 solutions in the presence (filled symbols) and absence (open symbols) of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_6OH (●,○) ; C_6NH_2 (▲,Δ).

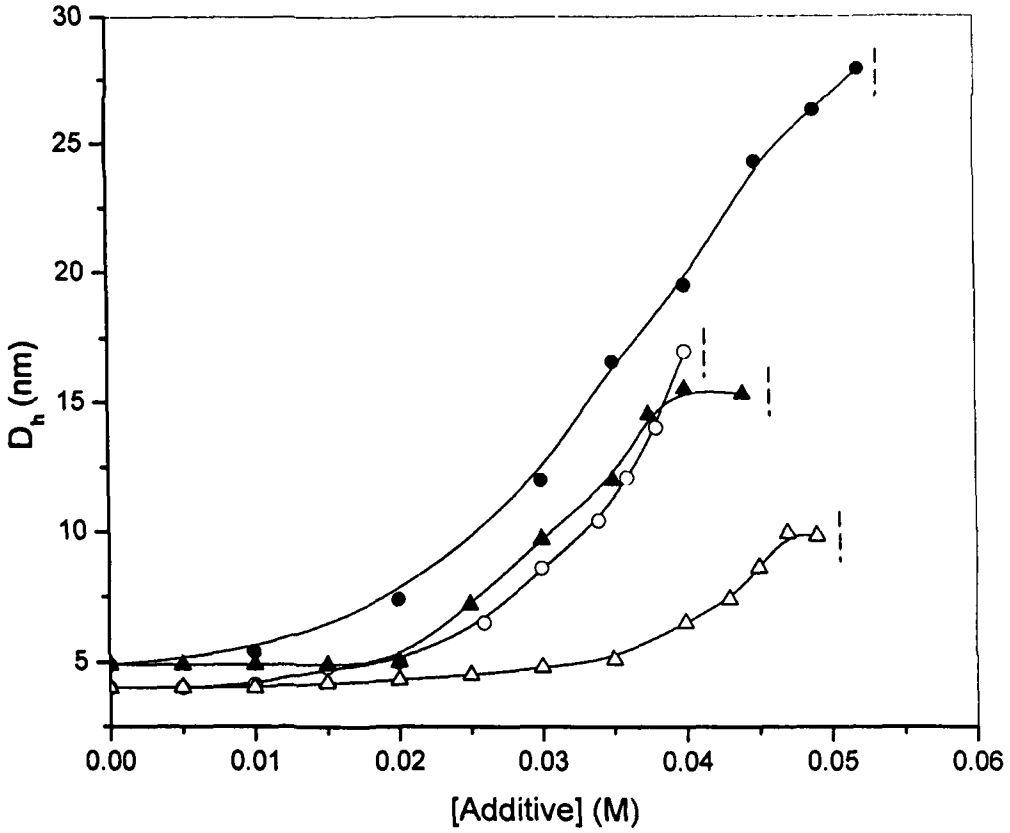


Fig.4.11(b). Variation of hydrodynamic diameter (D_h) with [additive] (of equal chain length) to 0.03 M 16–6–16 solutions in the presence (filled symbols) and absence (open symbols) of 0.005 M KBr at 30 °C (upto the solubility limit indicated by dotted lines): C_6OH (●,○) ; C_6NH_2 (▲,△).

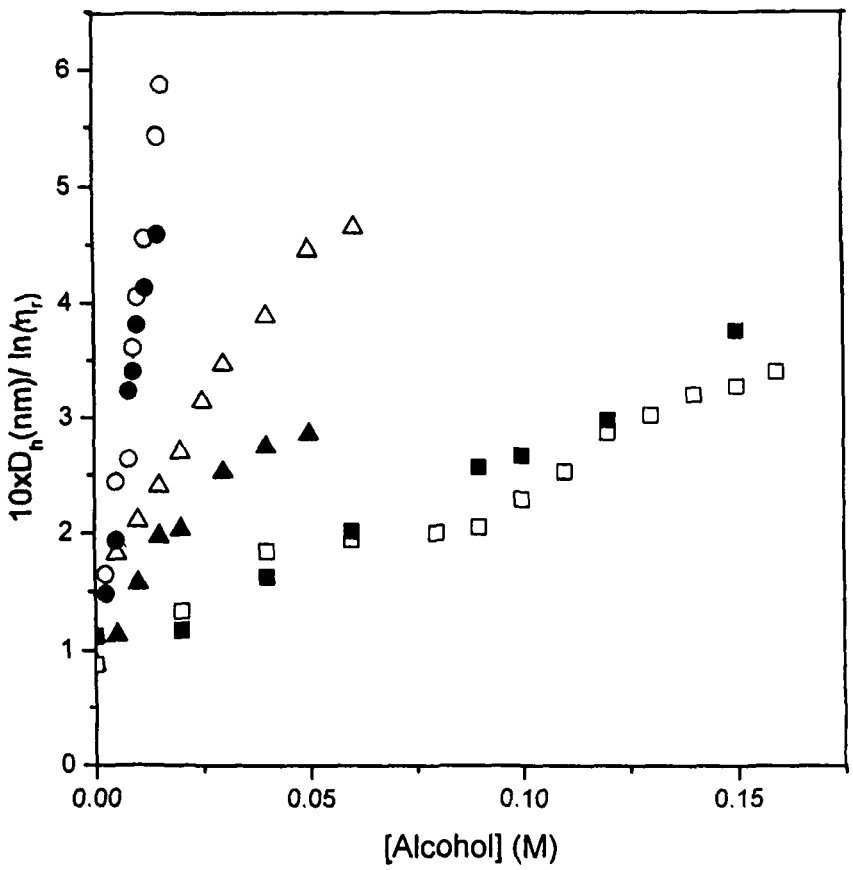


Fig. 4.12. Comparative data with added alcohols to 0.03 M 16-4-16 solutions in the presence of 0.001 M KBr at 30 °C obtained from DLS (filled symbols) and viscometry (open symbols): C_4OH (■,□); C_5OH (▲, Δ); C_6OH (●,○).

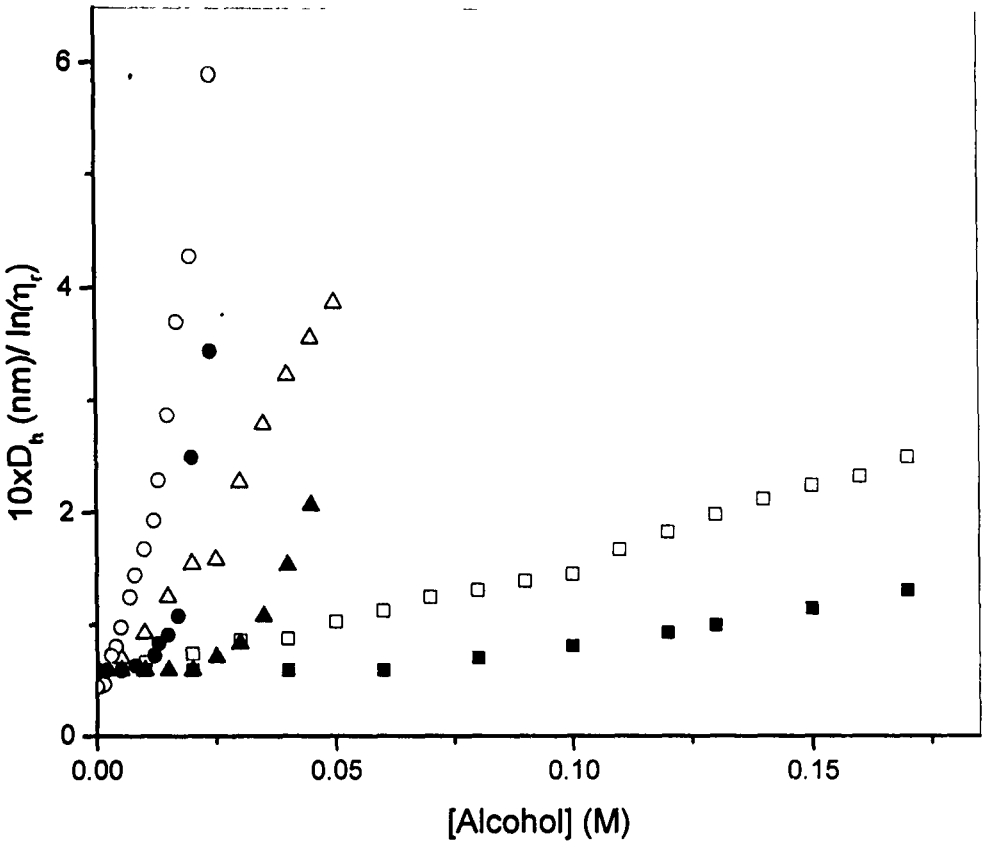


Fig. 4.13. Comparative data with added alcohols to 0.03 M 16-5-16 solutions in the presence of 0.005 M KBr at 30 °C obtained from DLS (filled symbols) and viscometry (open symbols): C_4OH (■,□); C_5OH (▲, Δ); C_6OH (●,○).

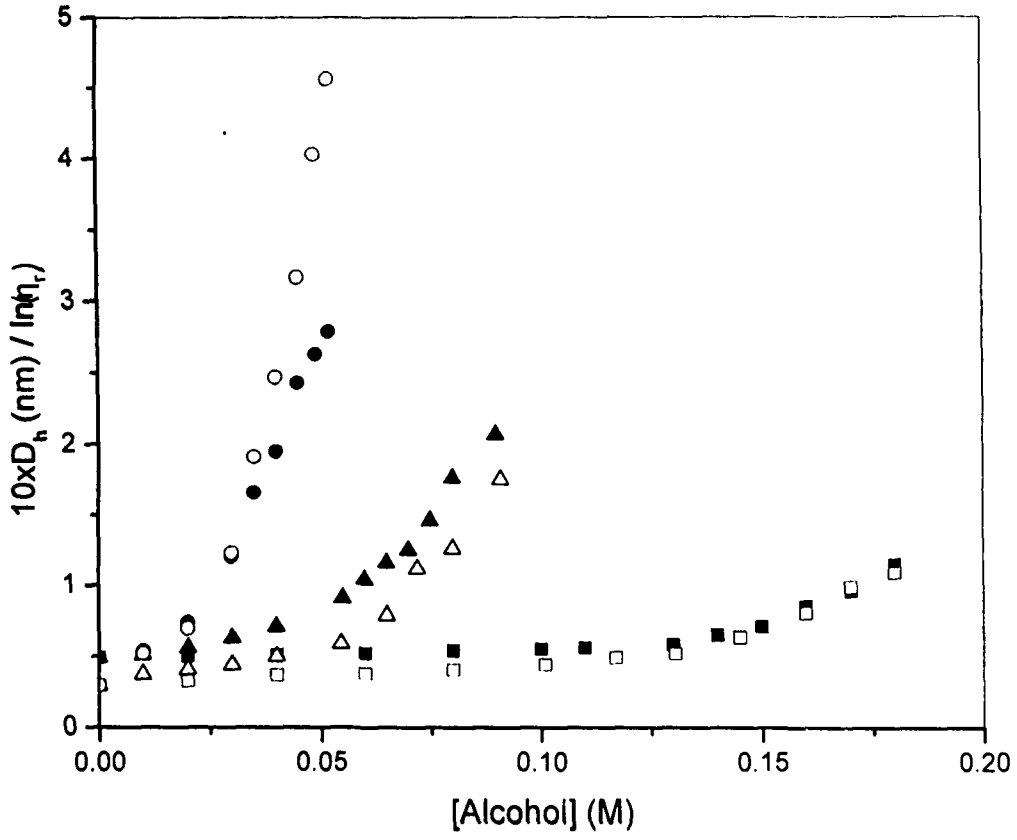


Fig. 4.14. Comparative data with added alcohols to 0.03 M 16-6-16 solutions in the presence of 0.005 M KBr at 30 °C obtained from DLS (filled symbols) and viscometry (open symbols): C_4OH (■,□); C_5OH (▲, Δ); C_6OH (●,○).

References

1. E. H. Lucassen-Reynders, J. Lucassen and D.Giles, *J. Colloid Interface Sci.*, **81**, 150 (1981).
2. D. Goralezyk, *Colloids Surf.*, **11**, 287 (1984).
3. J. A. McDonald and A. R. Rennie, *Langmuir*, **11**, 1493 (1995).
4. Kabir-ud-Din, D. Bansal and S. Kumar, *Langmuir*, **13**, 5071 (1997).
5. R. G. Alargova, I. I. Kochijashky, M. L. Sierra and R. Zana, *J. Colloid Interface Sci.*, **235**, 19 (2001).
6. S. Kumar, D. Sharma and Kabir-ud-Din, *Langmuir*, **19**, 3539 (2003).
7. S. Kumar, V. K Aswal, H. N. Singh, P. S. Goyal and Kabir-ud-Din *Langmuir*, **10**, 4069 (1994).
8. Kabir-ud-Din, S. Kumar, Kirti and P. S. Goyal, *Langmuir*, **12**, 1490 (1996).
9. Kabir-ud-Din, S. Kumar, V. K. Aswal and P. S. Goyal, *J. Chem. Soc., Faraday Trans.*, **92**, 2413 (1996).
10. S. Kumar, V. K. Aswal, P. S. Goyal and Kabir-ud-Din. *J. Chem. Soc., Faraday Trans.*, **94**, 761 (1998).
11. S. Kumar, D. Bansal and Kabir-ud-Din. *Langmuir* , **15**, 4960 (1999).
12. S. Kumar, A. Z. Naqvi and Kabir-ud-Din. *Langmuir*, **17**, 4787 (2001).

13. S. Kumar, N. Parveen and Kabir-ud-Din, *J. Phys. Chem. B*, **108**, 9588 (2004).

14. S. Kumar, D. Sharma and Kabir-ud-Din, *J. Surfactants Deterg.*, **6**, 339 (2003).

15. S. Kumar, D. Sharma, G. Ghosh and Kabir-ud-Din, *Colloids Surf. A*, **264**, 203 (2005).

16. S. Kumar, D. Sharma, G. Ghosh and Kabir-ud-Din, *Langmuir*, **21**, 9446 (2005).

17. T. Ahmad, S. Kumar, Z. A. Khan and Kabir-ud-Din, *Colloids Surf. A*, in press.

18. H. H. Kohler and J. Strnad, *J. Phys. Chem.*, **94**, 7628 (1990).

19. C. Gamboa and L. Sepulveda, *J. Colloid Interface Sci.*, **113**, 566 (1986).

20. H. Rehage and H. Hoffmann, *J. Phys. Chem.*, **92**, 4712 (1988).

21. H. Hoffmann and G. Ebert, *Angew. Chem. Int. Ed.*, **27**, 902 (1988).

22. G. M. Forland, J. Samseth, H. Hoiland and K. Mortensen, *J. Colloid Interface Sci.*, **164**, 163 (1994).

23. F. M. Menger and C. A Littau, *J. Am. Chem. Soc.*, **115**, 10083 (1993).

24. F. Devinsky, I. Lacko and T. Imam, *J. Colloid Interface Sci.*, **143**, 336 (1993).

25. Th. Dam, J. B. F. N. Engberts, J. Karthauser, S. Karaborni and N. M. Van Os, *Colloids Surf. A*, **118**, 41 (1996).

26. E. Buhler, E. Mendes, P. Boltenhagen, J. P. Munch, R Zana and S. J. Candau, *Langmuir*, **13**, 3096 (1997).

27. S. Ozeki and S. Ikeda, *J. Colloid Interface Sci.*, **77**, 219 (1980).

28. B. J. Berne and R. Pecora, "*Dynamic Light Scattering*; Wiley-Interscience": New York (1976).

29. S. W. Provencher, *Comput. Phys. Commun.*, **27**, 229 (1982).

30. D. Mukerjee,, "*Solution Chemistry of Surfactants*", Edited by K. L. Mittal, Plenum Press: New York, p 153 (1979).

31. S. De, V. K. Aswal, P. S. Goyal and S. Bhattacharya, *J. Phys. Chem.*, **100**, 11664 (1996).

32. R. Zana and Y. Talmon, *Nature*, **362**, 228 (1993).

33. D. Danino, Y. Talmon and R. Zana, *Langmuir*, **11**, 1448 (1995).

34. R. Zana, *Adv. Colloid Interface Sci.*, **97**, 205 (2002).

35. J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1525 (1976).

36. D. Oakenfull, *J. Colloid Interface Sci.*, **88**, 562 (1982).

37. M. Almgren and J. E. Lofroth, *J. Colloid Interface Sci.*, **81**, 486 (1981).

38. Z. Lin, J. J. Cai, L. D. Scriven and H. T. Davis, *J. Phys. Chem.*, **98**, 5984 (1994).

39. G. Hartel and H. Hoffmann, *Liq. Cryst.*, **5**, 1983 (1989).

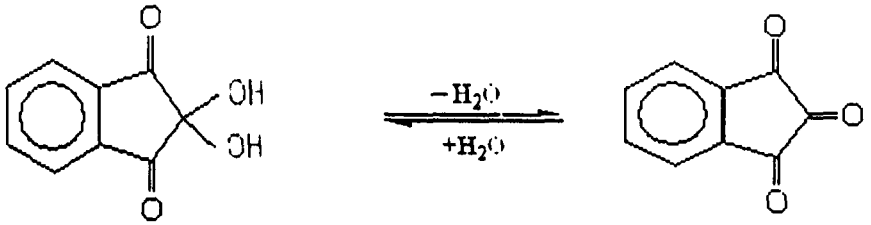
40. T.Yamashita, H.Yano, S. Harada andT. Yasunaga, *J. Phys. Chem.*, **87**, 5482 (1983).

Chapter-V

Kinetics of the L-Isoleucine-Ninhydrin Reaction in Aqueous and Micellar Media

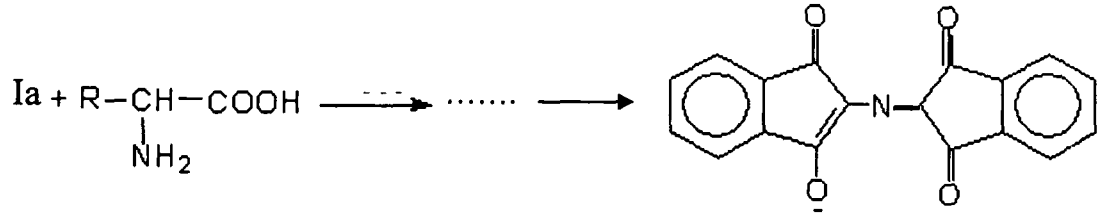
Introduction

The chemistry of ninhydrin-amine functionality reactions is of interest due to their application in bioanalytical work[1] and as latent fingerprint reagent.[1b,2] Since the use of ninhydrin (2, 2- dihydroxyindan-1, 3-dione, I, Eq. (5.1)) depends on the formation of purple-colored diketohydrindylidenediketo- hydrindamine (DYDA, the so-called *Ruhemann's purple*)[3] with an amine functionality (Eq. (5.2)), several aspects of the concerned reactions (some include even ninhydrin analogs) have been studied and discussed for many years.[1,4] Kinetic studies were, however, very limited.[5] With the view point that studies in this direction would be useful to understand the mechanistic aspects, we have reported systematic kinetic investigations of reactions of several amino acids with ninhydrin both in aqueous and aqueous-micellar



(5.1)

(I) (Ia)



(5.2)

(Ruhemann's purple)

Micellar solutions are known to affect the rates of chemical reactions and the positions of chemical equilibria.[7] It is generally accepted that ionic reactions occur at the micellar surface adjacent to the headgroups. Rate enhancements of biomolecular reactions by aqueous micelles, or similar colloidal assemblies, are due largely to bringing together of both reactants in the small volume of the micelles. The hydrophobic and electrostatic factors play an important role in the micellar catalysis. Out of these two factors, hydrophobic effect is the most important in the organization of the constituent molecules of the living matter into complexes.

The present work was undertaken in the hope that introduction of $CH_3\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{–}$ group (hydrophobic) into the side chain of amino acid L-isoleucine would assist in its binding to micelles. A systematic kinetic study of the title reaction has, therefore, been made in sodium acetate-acetic acid buffer both in aqueous and cationic micellar (CTAB and geminis) media. The effects of some polar organic solvents have also been explored.

It has already been established that reactant concentrations, pH, and temperature all play an important role in the formation of purple-colored product.[4b] At fixed [amino acid] and pH, the absorbance due to purple

color increases with temperature and reaches a stationary state at each temperature.

In order to see the role of cationic surfactants, experiments were performed under different experimental conditions in aqueous and micellar media. For the sake of simplicity the results are discussed in three parts.

Results and Discussion

A. Reaction in the absence of surfactant:

***Product identification*:** No color formation was observed under the conditions of [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, pH = 5.0, and temperature = 80 °C. But when we increased the reactant concentrations, i.e., [L-isoleucine] = 6.0×10^{-4} mol dm^{-3}, and [ninhydrin] = 10.0×10^{-3} mol dm^{-3} at the same pH and temperature, the reaction did occur with the formation of the purple-colored product. To characterize the formation of reaction product, i. e., *Ruhemann's purple* (λ_{max} = 390 nm and 570 nm), [1,6] absorption spectra of the reaction mixture containing [L-isoleucine] = 6.0×10^{-4} mol dm^{-3}, [ninhydrin] = 10.0×10^{-3} mol dm^{-3} at pH = 5.0 were recorded at the end of the reaction under different experimental conditions. Fig. 5.1(a) shows that at 80 °C the reaction in aqueous medium can be followed spectrophotometrically.

Kinetics: To compare the reactivity of L-isoleucine in aqueous as well as in micellar media, it is necessary to see the effect of variables in the

absence of surfactant. First of all, the effect of pH was seen in the range 3.7 to 5.9. Values of the pseudo-first-order rate constants (k_{obs}) are summarized in Table 5.1. It was observed that the k_{obs} increased upto pH = 5.0 and thereafter became almost constant (Fig. 5.2). Every elementary reaction of the α-amino acids and ninhydrin depends upon the hydrogen ion concentration because the reaction proceeds through the formation of an intermediate which has Schiff base linkage (> C = N–).[1] The end product (*Ruhemann's purple*) of this reaction also has this type of linkage. The Schiff base formation is acid catalysed and pH = 5.0 is the optimum pH.[1,6a,6b] Therefore, all the kinetic measurements were performed at pH = 5.0. The reaction was then studied as a function of [L-isoleucine] between 5-7 x 10^{-4} mol dm^{-3} at fixed [ninhydrin] = 10.0 x 10^{-3} mol dm^{-3} and pH = 5.0 at 80 °C. The independence of rate constants over the range of [L-isoleucine] (Table 5.1) is in agreement with a first-order dependence on [L-isoleucine], indicating that the total L-isoleucine must be used in the rate law. Hence, the rate of the reaction can be represented as

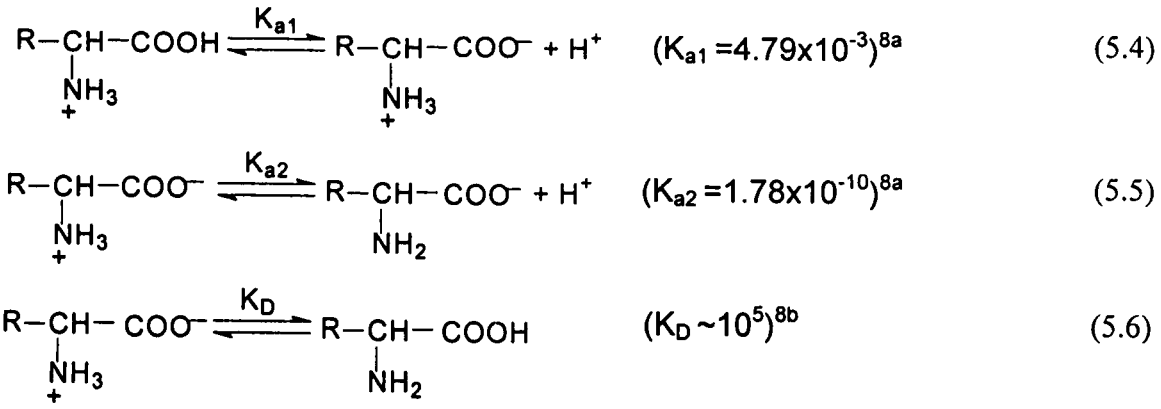
$$d[P]/dt = k_{obs}\,[\text{L-isoleucine}]_T \qquad (5.3)$$

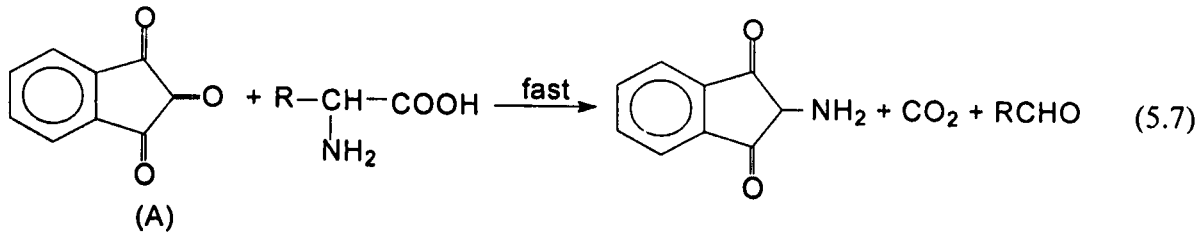
The effect of [ninhydrin] on the k_{obs} is also summarized in Table 5.1. A plot of k_{obs} versus [ninhydrin] is curved, passing through the origin (Fig. 5.3). However, a double-logarithmic plot between k_{obs} and

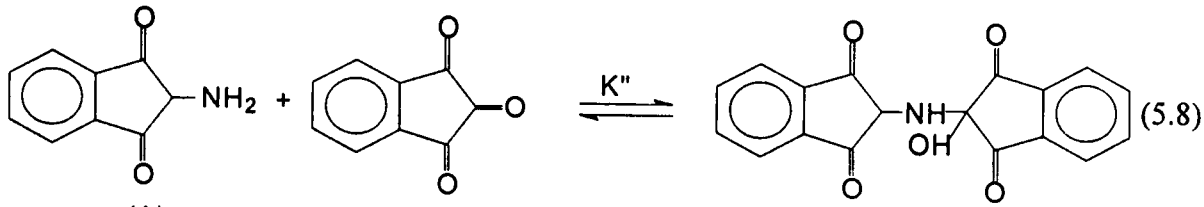
[ninhydrin] yielded a straight line with slope < 1 indicating that the order with respect to [ninhydrin] is fractional. On the other hand, Michaelis-Menten behavior, a k_{obs}^{-1} versus $[ninhydrin]^{-1}$ plot, was also linear with a positive intercept on y-axis.

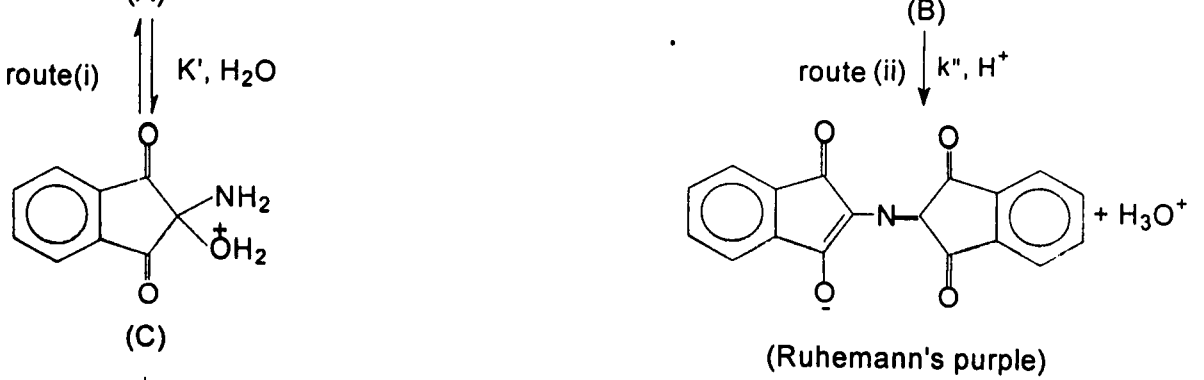
The kinetic data obtained at different temperatures are presented in Table 5.2. The logarithm of k_{obs} showed a linear dependence on 1/T, indicating that the reaction follows the Eyring and Arrhenius relationships.

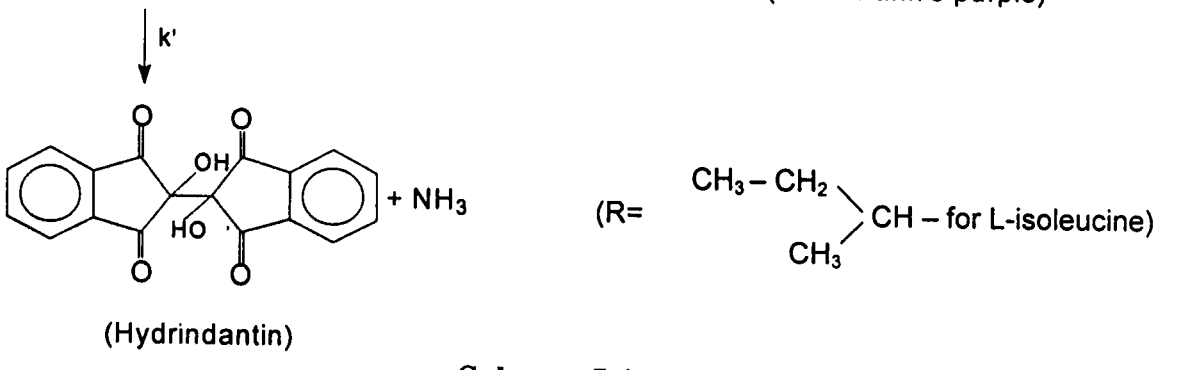
The general mechanism of ninhydrin–amino acid reactions in aqueous medium (pH range: 4.0 – 5.5) is given as Scheme 5.1.[1a] It is known that, on interaction of α-amino acids with ninhydrin, carbon dioxide, aldehyde, ammonia, hydrindantin and *Ruhemann's purple*[1a] are produced. The reaction proceeds through the formation of a Schiff's base which further undergoes decarboxylation and hydrolysis to yield 2-amino-indanedione **(A)** as a stable intermediate. **A** undergoes two processes which occur simultaneously: (i) hydrolysis, and (ii) condensation; as a result, NH_3 and *Ruhemann's purple* are the respective products. This reaction is strongly influenced by the reaction conditions, i.e., pH, temperature and [ninhydrin] and also on presence of atmospheric oxygen. In the presence of atmospheric oxygen, a yellow-colored product is formed (instead of purple-colored). At low pH, the reaction proceeds mainly by


R–CH–COOH ⇌ R–CH–COO⁻ + H⁺ (K_{a1} =4.79x10^{-3})[8a] (5.4)
NH3+
R–CH–COO⁻ ⇌ R–CH–COO⁻ + H⁺ (K_{a2} =1.78x10^{-10})[8a] (5.5)
NH3+ NH2
R–CH–COO⁻ ⇌ R–CH–COOH (K_D ~10^5)[8b] (5.6)
NH3+ NH2


+ R–CH–COOH
NH2
fast
NH2 + CO2 + RCHO (5.7)
(A)


NH2 +
K"
NH
OH
(5.8)
(A)
(B)


route(i)
K', H2O
route (ii)
k", H+
NH2
OH2
+ H3O+
(C)
(Ruhemann's purple)


k'
OH
HO
+ NH3
(R= CH3 – CH2 CH – for L-isoleucine)
CH3
(Hydrindantin)

Scheme 5.1

route(i) and ammonia is evolved with no *Ruhemann's purple* formation. In solutions of pH≥5.0, route(ii) predominates but there may be some possibility of route (i) also.

Formation of Schiff base between the carbonyl group of ninhydrin and the amino group of L-isoleucine doesn't allow cationic R-CH(N^+H_3)COOH and zwitterionic R-CH(N^+H_3)COO^- species to attack the middle carbonyl group of ninhydrin.[1a,6d-f,m,n,9] Due to the presence of positive charge on the amino group, the nucleophilic character of amino nitrogen is diminished, hence they are kinetically inactive. Thus, R-CH(NH_2)COOH and R-CH(NH_2)COO^- may be considered as the reactive species. Under our experimental conditions, [R-CH(NH_2)COO^-] is negligible because of very low pK_{a2} (9.758) and high K_D values.[8] The reactive species towards the nucleophilic attack on the >C=O group of ninhydrin is therefore R-CH(NH_2)COOH, which is in equilibrium with the zwitterionic form of L-isoleucine.[8b] As regards ninhydrin, though the equilibrium states I and Ia exist in aqueous solution (Eq. (5.1)), Ia has been found as the reactive species for condensation.[9]

B. Reaction in the presence of CTAB:

Product identification: Under the same conditions, the presence of CTAB micelles also could not affect the reaction as in this case also r purple color developed under concentrations of [L-isoleucine] = $1.0x10^{-4}$ mol dm^{-3}, [ninhydrin] = $5.0x10^{-3}$ mol dm^{-3}, [CTAB] = $20.0x10^{-5}$ –

$20.0x10^{-3}$ mol dm^{-3} at 80 °C. Again, on increasing the reactant concentrations, e.g., [L-isoleucine] = $6.0x10^{-4}$ mol dm^{-3}, [ninhydrin] = $10.0x10^{-3}$ mol dm^{-3} (at the same pH and temperature), the purple-colored product was well formed with λ_{max} = 570 nm (Fig. 5.1(b) & (d)). This confirms that the product (*Ruhemann's purple*) remains unchanged with the change in the reaction medium from aqueous to micellar phase. Also, at 80 °C, the absorbance is higher in CTAB than in the aqueous medium. These results are in conformity that there is a strong association between the purple-colored product and CTAB micelles. Another possibility is that side reactions are blocked in the presence of CTAB which, in turn, suppress the loss of amino nitrogen (see Scheme 5.1).

Kinetics: The effect of CTAB micelles upon the absorbance and reaction rate was seen at fixed [ninhydrin] = 10.0×10^{-3} mol dm^{-3}, [L-isoleucine] = 6.0×10^{-4} mol dm^{-3}, and pH = 5.0 at 80 °C. The rate constant in micellar media, k_ψ, increased from 4.3 to 9.6×10^{-5} s^{-1} with increase in [CTAB] from 0 to 70.0×10^{-3} mol dm^{-3}. These results are summarized in Table 5.3. The k_ψ–[CTAB] profile shape (Fig. 5.4) is perfectly general being a common feature of bimolecular reactions catalyzed by micelles.[7c,10-12]

Further, absorbance (due to purple color) also increases with [CTAB], indicating association and/or incorporation of the purple-colored product with the CTAB micelles. It has been reported that presence of micelles can alter the mechanism of reactions.[13] Therefore, in order to

confirm the Scheme 5.1 mechanism, the effects of [L-isoleucine], [ninhydrin], pH and temperature were seen in the presence of 40.0×10^{-3} mol dm^{-3} CTAB too (Tables 5.1–5.3, Figs. 5.2 & 5.3). The same first- and fractional-order kinetics with respect to [L-isoleucine] and [ninhydrin] were followed. Thus, taking cognizance of the absorption band of the purple-colored product also remaining unchanged in presence of the CTAB, we conclude that the reaction mechanism remains the same in the presence of CTAB micelles as that in aqueous medium.

For the evaluation of activation parameters, a series of kinetic runs were carried out in the temperature range 75–90 °C. The values of k_ψ were found to fit the Arrhenius and Eyring equations:

$$k_\psi = A \exp(-E_a/RT) \qquad (5.9)$$

$$k_\psi = [k_B T/h] \exp[-\Delta H^{\neq}/RT] \exp[\Delta S^{\neq}/R] \qquad (5.10)$$

where all the symbols have their usual meanings. The values of E_a, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are given in Table 5.2. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are substituted in Eq. (5.10) and k_{cal} values are calculated (Table 5.2). The clear agreement between the rate constants (observed) and rate constant (calculated) provides the supporting evidence for the observed data. The large decrease in $\Delta S^{\neq}$ shows that the transition state is well structured in the micellar phase.

C. Reaction in the presence of geminis :

Product identification: Under the reaction conditions of [L-isoleucine] = $1.0x10^{-4}$ mol dm^{-3}, [ninhydrin] = $5.0x10^{-3}$ mol dm^{-3}, pH = 5.0 at 80 °C, where no color developed in aqueous or in the presence of CTAB micelles, a small concentration (below cmc) of the geminis was sufficient to accelerate the rate of the reaction. In order to confirm whether the same colored product is formed in the absence and presence of surfactants (CTAB, geminis), absorption spectra of the reaction mixture, i.e., [L-isoleucine] = $1.0x10^{-4}$ mol dm^{-3}, [ninhydrin] = $5.0x10^{-3}$ mol dm^{-3}, [gemini] = $20.0x10^{-5}$ mol dm^{-3} and pH = 5.0 at 80 °C, were taken at the end of the reactions. These results are shown as absorbance-wavelength profiles in Figs. 5.5–5.7. The absorption maxima were found at λ_{max} = 390 nm and 570 nm, which clearly indicate that the same purple-colored reaction product (*Ruhemann's purple*) is formed in each case due to the strong association between the product and gemini micelles. No change in the absorption maxima in the absence as well as presence of CTAB/gemini surfactants/solvents leads to the conclusion that the same product is formed in each case (Figs. 5.5–5.7).

Kinetics: A detailed account of our study on all the three gemini surfactants is given below.

Effect of pH. As before, the effect of pH on the reaction was seen by varying the pH (range: 3.5 – 6.0) at constant [L-isoleucine] = $1.0x10^{-4}$ mol

dm^{-3}, [ninhydrin] = $5.0x10^{-3}$ mol dm^{-3}, and [16-*s*-16] = $20.0x10^{-5}$ mol dm^{-3} at 80 °C. The respective k_ψ values are given in Table 5.4 (Fig. 5.8). Once again pH = 5.0 is the optimum and, therefore, all the subsequent kinetic measurements were made at pH = 5.0.

Effect of [L-isoleucine]. To find the order of the reaction with respect to [L-isoleucine], k_ψ were determined at different [L-isoleucine] from $1.0 - 3.5x10^{-4}$ mol dm^{-3} in presence of [16-*s*-16] = $20.0x10^{-5}$ mol dm^{-3} at constant [ninhydrin] = $5.0x10^{-3}$ mol dm^{-3}, pH = 5.0, and temperature = 80 °C (Table 5.4). It was observed that the values of k_ψ were independent of the initial [amino acid], which confirms the order of the reaction with respect to [L-isoleucine] to be unity (see Eq. (5.3)).

Effect of [ninhydrin]. In presence of 16-*s*-16 gemini micelles, the rate constants were obtained at different [ninhydrin], varying from $5.0 - 40.0x\ 10^{-3}$ mol dm^{-3}, at constant [L-isoleucine] at pH 5.0 and 80 °C. The results are given in Table 5.4. Plots of k_ψ vs. [ninhydrin] are nonlinear passing through the origin (Fig. 5.9), whereas double-logarithmic plots between k_ψ vs. [ninhydrin] yielded straight lines with slopes less than unity, indicating fractional - order with respect to [ninhydrin].

Effect of [gemini]. The rate constants (k_ψ) were determined at several gemini surfactant concentrations under the reaction conditions of [L-isoleucine] = $1.0x10^{-4}$ mol dm^{-3} and [ninhydrin] = $5.0x10^{-3}$ mol dm^{-3} at

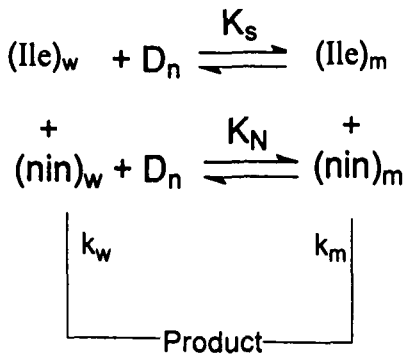
pH = 5.0 and temp.= 80 °C (Table 5.5). Variations of k_ψ as a function of the concentrations of 16-*s*-16 (*s* = 4, 5, 6) are shown in Fig. 5.10. It can be seen that the values of k_ψ for the reaction increase progressively with increasing surfactant concentration upto about ~20.0 $x10^{-5}$ mol dm^{-3}, become almost constant and then increase again. Values of pseudo-first-order rate constants generally become approximately constant when a substrate is fully micellar bound with the micellar structure considered to remain unaltered.[7c,14] After leveling-off, further increase at higher [gemini] is probably associated with a change of micellar structure. That structural changes indeed occur at higher [gemini] are confirmed by examining the ^1H NMR spectra of the surfactants. Whereas chemical shifts with concentrations of surfactants remain almost invariant,[15] increases of line width at half-height (lw) signals of hydrogens of $-N^+CH_3$ segment are seen (Table 5.6). The broadening is consonant with the literature evidence for transition to larger aggregates.[16,17] Obviously, changes in aggregate morphology provide different reaction microenvironments (less polar), hence the k_ψ values increase sharply (Fig. 5.10).

This is true for all the gemini micelles, only the extent of increase in k_ψ is different depending on the spacer chain length.

Effect of spacer chain length. The influence of spacer chain length variation (*s*-value) on the reaction rate of the formation of the purple-

colored product under comparable reaction conditions is illustrated in Fig. 5.11, which shows maximum k_ψ at $s = 4$. It is known that length and type of the spacer moiety dictates the conformation of the gemini molecule.[18] The micellar growth is more pronounced the shorter the spacer unit, which is most likely due to the increasing geometrical constraints in the formation of aggregates with decreasing length of the spacer unit. Microviscosity and SANS data also support the argument that, within the gemini surfactants, micellar morphology tends to be less ellipsoidal with increasing s.[19] Thus, because of the spacer greatly influencing the surfactant morphology, the k_ψ values obtained in the present studies are consistent with the expectation being maximum at $s = 4$.

The observed catalytic role of micelles (CTAB and geminis) may be explained in terms of the modified pseudo-phase model [11,12] (Scheme 5.2) originally proposed by Menger and Portnoy.[10]



Scheme 5.2

where w and m represent the aqueous and micellar pseudophase, respectively, and D_n is the micellized surfactant. The observed rate equation, $\nu = k_\psi$ [L-isoleucine]$_T$, and Scheme 5.2 yield Eq. (5.13)

$$k_\psi = \{k_w + k_m K_S[D_n]\} / (1+K_S[D_n]) \qquad (5.13)$$

where $[D_n]$ = [micelle] minus cmc and k_w and k_m the pseudo-first-order rate constants. As the k_ψ – [surfactant] profiles show characteristics of a bimolecular reaction, Eq. (5.13) is modified as Eq. (5.14)

$$k_\psi = \{k'_w[(nin)_w] + (K_S k'_m - k'_w) M_N^S [D_n]\} / (1+K_S[D_n]) \qquad (5.14)$$

where $k'_w = k_w / [(nin)_w]$ and $k'_m = k_m / M_N^S$ (k'_w and k'_m are the second-order rate constants and M_N^S (= $[(nin)_m]/[D_n]$) is the mole ratio of ninhydrin bound to the micellar headgroup). Considering Scheme 5.2 in conjunction with the mass balance on ninhydrin,[20] we obtain quadratic Eq. (5.15)

$$K_N[(nin)_m]^2 - (K_N[D_n] + K_N[(nin_T)] + 1)[(nin)_m] + K_N[D_n][(nin)_T] = 0 \qquad (5.15)$$

Eq. (5.15) was solved for $[(nin)_m]$ with the help of a computer program with K_N as an adjustable parameter. For calculation, we need the cmc values which were determined by conductivity method under the kinetic experimental conditions (Table 5.7). The values of k'_m and binding

constant K_S were calculated using a non-linear least squares technique and are given in Table 5.8. Substituting these values in Eq. (5.14), (or, in its modified form, $k_\psi = \{K_S\, k'_m\, M_N^S\, [D_n]\}/(1+K_S[D_n])$, for the case of gemini surfactant where no purple color developed, i. e., $k'_w = 0$, under the experimental conditions used therein). Calculated values ($k_{\psi,cal}$) were obtained (Tables 5.3 & 5.5) which show good agreement with the experimental k_ψ; this can be taken as supporting evidence for the method used.

Effect of solvents. The effect of the addition of organic solvents; 1-propanol (PrOH), methyl cellosolve (MC), acetonitrile (AN) and dimethylsulfoxide (DMSO) in the gemini micellar media on the reaction rate was observed at [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3}, mol dm^{-3} [16-*s*-16] = 20.0×10^{-5} mol dm^{-3}, and pH = 5.0 at 80 °C.

As before,[6i-m] the addition of water-soluble organic solvents markedly increased the rate as well as the intensity of color (Tables 5.9–5.11, Figs. 5.12-5.14,). The solvents used in this study, which mainly affect the properties of the bulk water, belong to three different categories: (1) alcohols (PrOH and MC) which are responsible for enhancing micellization at very low concentrations and inhibiting it at higher concentrations, (2) AN which forms strong hydrogen bonds with water, and (3) DMSO which forms hydrates with water.[21] Each solvent has been found to postpone micellization of the gemini surfactants due to

different reasons (Chapter – I). In case of PrOH and MC, the destruction of the original water's 3D structure occurs and, as a result, new H-bonds between water and alcohols are formed.[21] These alcohol-water mixtures are better solvents for gemini micelles than pure water and effective number of micelles thus decrease. Similarly, the decrease in the number of micelles in presence of AN is due to the formation of H-bonds between water and AN molecules. The effect of DMSO on gemini micellization can be explained on the basis of strong interaction with water and stiochiometric hydrate ($DMSO.2H_2O$) formation which results in increased structuring of the solvent system.[21]

Despite all the four solvents inhibiting the micellization in geminis, the reaction is still catalyzed in presence of these solvents. This can be due to the relative participation of water and organic solvents in acid-base equilibria and hydrogen bonding. It is already reported[22] that pH of the medium and pK_{a2} – values of amino acids are directly related to the rate enhancements in the reactions of α-amino acid - ninhydrin in presence of non-aqueous organic solvents. Our observations indicate that there is no major change in the pH of the working solutions in presence of these solvents.[6m] Therefore, the unique behavior of the organic solvents can be explained by the fact that an increase in the solvent volume decreases the water content in a given set, which decreases the rate of hydrolysis (route (i) of Scheme 5.1). In this way, the oxidative side reaction is

progressively blocked with an increase in the organic solvent content. Higher solubility of *Ruhemann's purple* in organic solvents[6a,b] imparts increased intensity. Thus, in presence of organic solvents, the blockage of the side reaction(s) (mainly hydrolysis) and higher solubility of the product play important roles.

Probable Role of Micelles: Hydrophobic and electrostatic interactions are the main factors in the kinetic micellar catalysis, which increase the concentration of reactants into a small volume. The properties of interfacial and bulk water play an important role in micellar effects on chemical equilibria and reaction rates. The interfacial water is less polar and more structured than bulk water.[23,24] The cationic micelles arrest water molecules in the polar region (Stern layer). As the micelles are cationic, hydrophobic and electrostatic interactions are considered. The hydrophobic chain $CH_3\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{–}$ of L-isoleucine is responsible for its incorporation into the micelles. On the other hand, electrostatic interactions between the positive headgroup of the cationic micelles and COO^- moiety of the reactive L-isoleucine species (see Eq. (5.6)) may also play an important role in concentrating the reactant into a small volume. The possibility of the electrostatic interactions between the micelles and electron rich moiety of ninhydrin can not be ruled out either. Thus the micelles play the role of concentrating the reactant species by localizing

them into the small micellar head group region thereby catalyzing the reaction due to 'proximity effects'.

The dicationic gemini micelles provide much better environment for ninhydrin- L-isoleucine reaction as compared to their corresponding monocationic counterpart CTAB micelles. It is known that the spacer chain at head group level of geminis decrease the extent of water penetration at the micellar surface: this could be the reason of kinetic advantages of the geminis used in the present studies. In addition to typical rate constant increase and leveling off regions (just like conventional CTAB), an unusual third region of increasing k_ψ at [16-*s*-16]≥ 60xcmc was observed. ^{1}H NMR, studies reveal the formation of larger aggregates at these higher surfactant concentrations which provide less polar environment and hence k_ψ increases. Based on the above, the ninhydrin- L-isoleucine reaction can thus be used as a simple and reliable kinetic probe in aggregate structures.

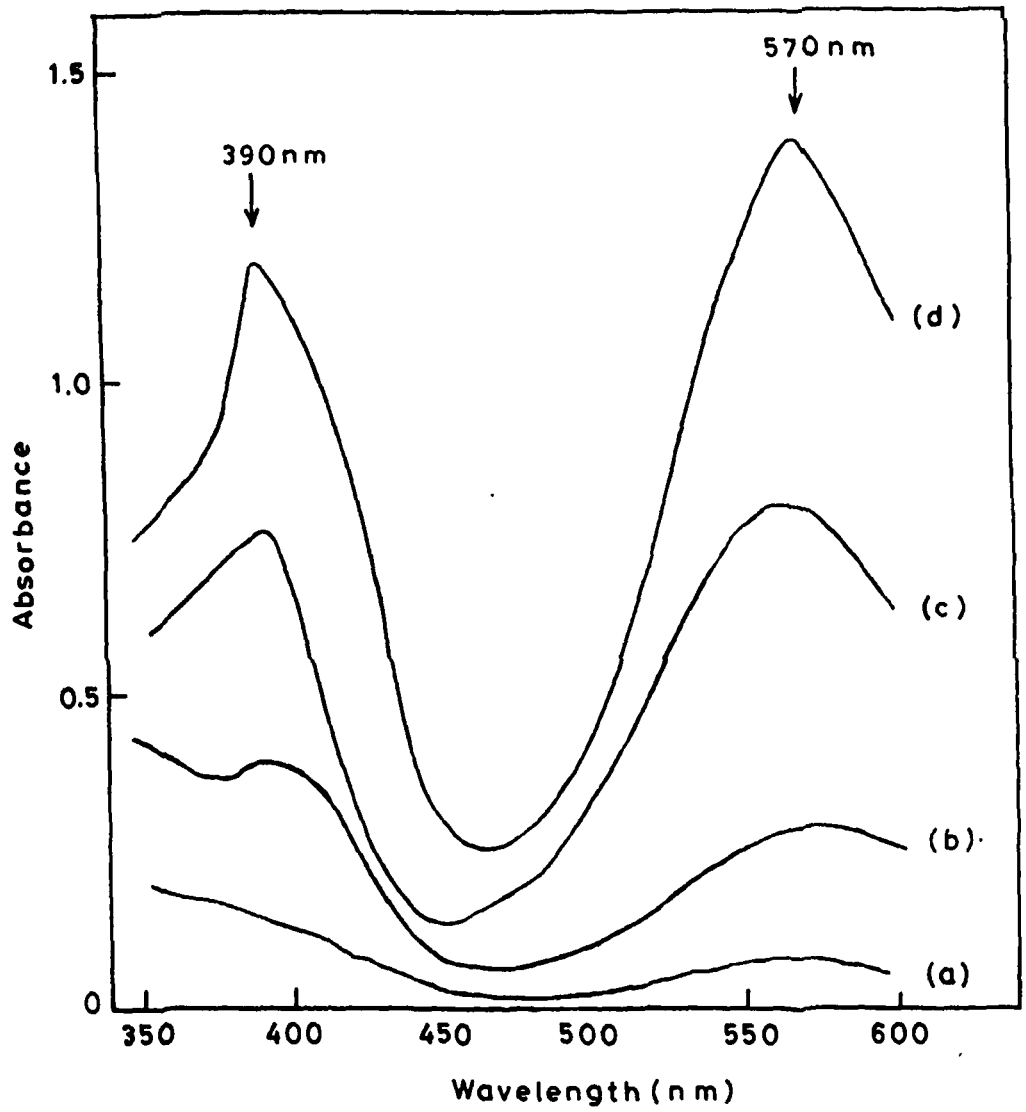


Fig. 5.1. Absorption spectra of Ruhemann's purple formed by the reaction of L-isoleucine and ninhydrin in the absence and presence of CTAB (a) after heating the reactant mixture at 80 ^{0}C for 1hr, (b) same as solution (a) in presence of [CTAB]=40.0x10^{-3}, (c) after boiling solution (a) and (b) after solution (b) [ninhydrin]= 10.0x10^{-3} mol dm^{-3} [L-isoleucine] =6.0x10^{-4} mol dm^{-3}, pH =5.0.

Table 5.1: Dependence of rate constants on pH, [L-isoleucine] and [ninhydrin] in the absence and presence of CTAB (=40.0x10^{-5} mol dm^{-3}) at 80 °C.

10^4[L-isoleucine] (mol dm^{-3})	10^3[ninhydrin] (mol dm^{-3})	pH	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_\psi$ (s^{-1})
6.0	10.0	3.7	1.5	3.5
6.0	10.0	4.0	2.0	3.9
6.0	10.0	4.5	2.3	5.5
6.0	10.0	5.0	4.3	9.3
6.0	10.0	5.4	4.5	10.2
6.0	10.0	5.9	4.8	10.6
5.0	10.0	5.0	4.5	9.2
5.5	10.0	5.0	4.9	9.4
6.0	10.0	5.0	4.3	9.3
6.5	10.0	5.0	4.3	9.4
7.0	10.0	5.0	4.4	9.4
6.0	10.0	5.0	4.3	9.3
6.0	15.0	5.0	7.5	15.3
6.0	20.0	5.0	11.6	22.5
6.0	25.0	5.0	14.9	26.9
6.0	30.0	5.0	17.5	35.5
6.0	35.0	5.0	20.6	39.9
6.0	40.0	5.0	22.6	42.5
6.0	45.0	5.0	23.6	43.0

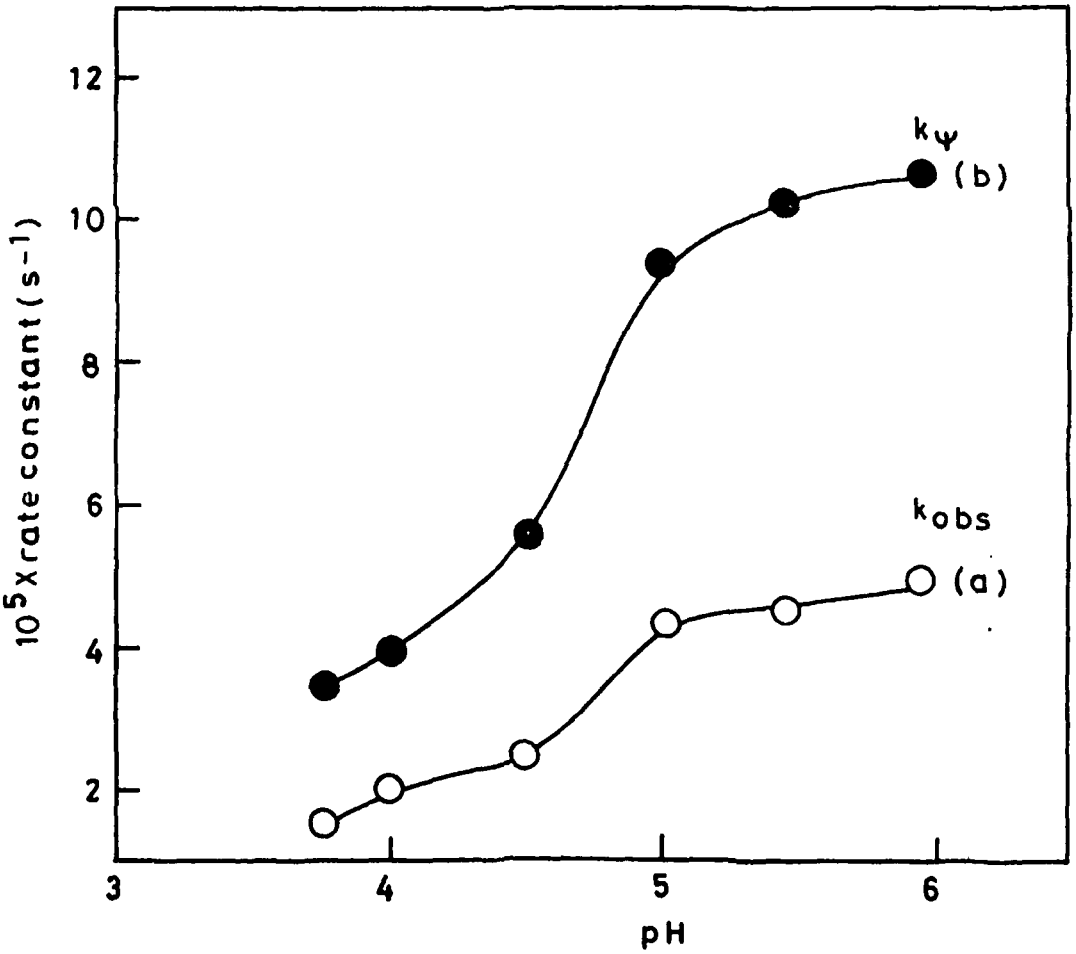


Fig. 5.2. Rate constant–pH profiles for the reaction of [L-isoleucine] =6.0×10^{-4} mol dm^{-3} and [ninhydrin]= 10.0×10^{-3} mol dm^{-3} at 80 ^{0}C in the absence (k_{obs}) and presence (k_ψ) of [CTAB]= 40.0×10^{-3} mol dm^{-3}.

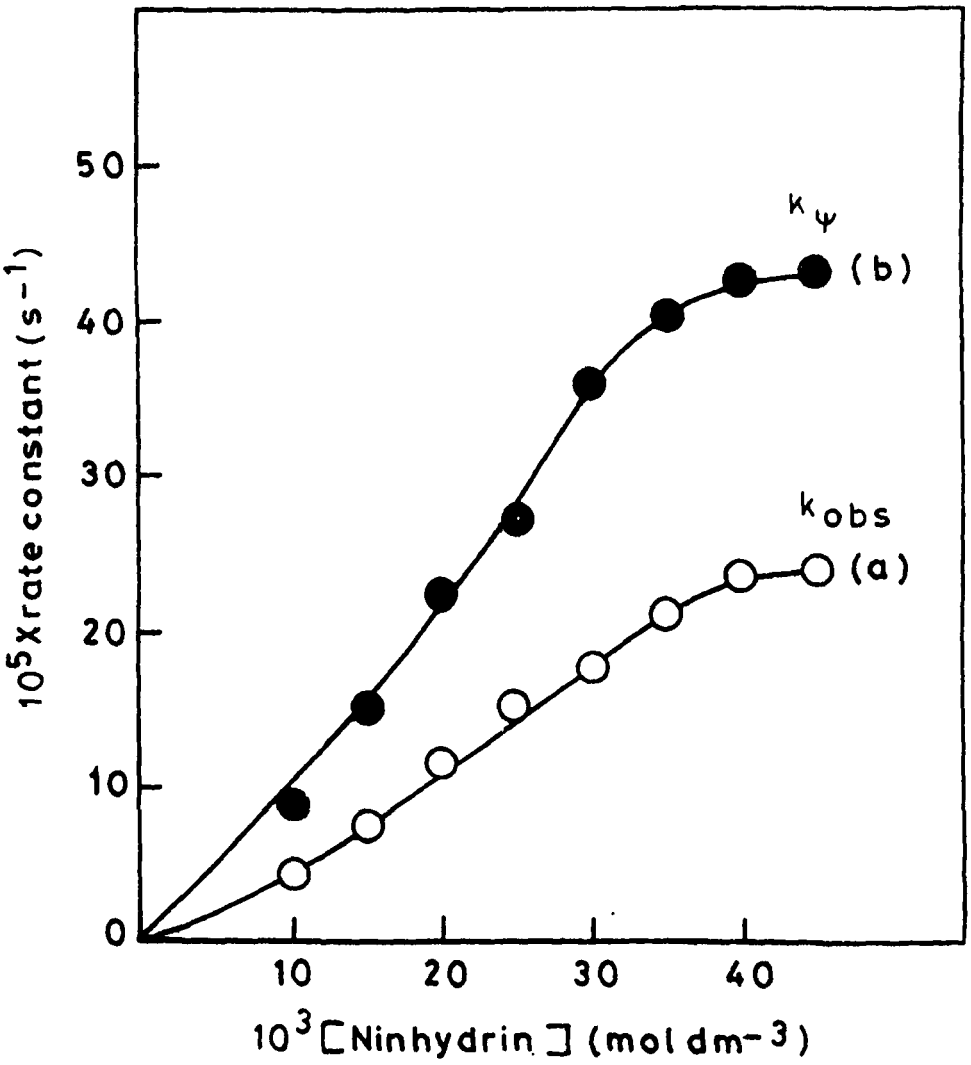


Fig.5.3. Plots of rate constant vs. [ninhydrin].(a) [L-isoleucine]= 6.0x 10^{-4}mol dm^{-3}, pH =5.0 temp. = 80 ^{0}C; (b) same as in (a) with [CTAB]= 40.0 x 10^{-3} mol dm^{-3}.

Table 5.2: Dependence of rate constants on temperature and related activation parameters for the L-isoleucine (=6.0×10^{-4} mol dm^{-3}) – ninhydrin (=10.0×10^{-3} mol dm^{-3}) reaction in the absence and presence of CTAB (=40.0×10^{-5} mol dm^{-3}) at pH 5.0.

Temperature (°C)	Aqueous			CTAB		
	$10^5 k_{obs}$ (s^{-1})	$10^5 k_{cal}$ (s^{-1})	$\frac{k_{obs} - k_{cal}}{k_{obs}}$	$10^5 k_{\psi}$ (s^{-1})	$10^5 k_{\psi,cal}$ (s^{-1})	$\frac{k_{\psi} - k_{\psi,cal}}{k_{\psi}}$
70	no reaction			no reaction		
75	3.3	3.7	–0.12	7.9	7.8	+0.01
80	4.3	4.8	–0.12	9.3	9.5	–0.02
85	5.8	5.9	–0.02	11.2	11.2	+0.00
90	7.3	7.4	–0.01	14.1	13.8	+0.02
Activation Parameters						
E_a (kJ mol^{-1})	47.9			39.8		
$\Delta H^{\neq}$ (kJ mol^{-1})	44.9			36.9		
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	–202.0			–219.0		

Table 5.3: Dependence of rate constants on [CTAB] for the reaction of ninhydrin (=10.0x10^{-3} mol dm^{-3}) with L-isoleucine (=6.0x10^{-4} mol dm^{-3}) at constant pH (5.0) and temperature (80 °C).

10^5 [CTAB] (mol dm^{-3})	10^5 k_ψ (s^{-1})	10^5 $k_{\psi,cal}$ (s^{-1})	$\frac{k_\psi - k_{\psi,cal}}{k_\psi}$
0.0	4.3	4.3	+0.0
5.0	5.2	4.8	+0.08
10.0	6.3	7.0	–0.11
15.0	6.9	10.1	–0.46
20.0	7.6	11.0	–0.45
25.0	7.8	10.9	–0.40
30.0	8.7	10.6	–0.22
40.0	9.3	8.8	+0.05
50.0	9.5	8.4	+0.11
60.0	9.6	7.5	+0.22
70.0	9.6	5.8	

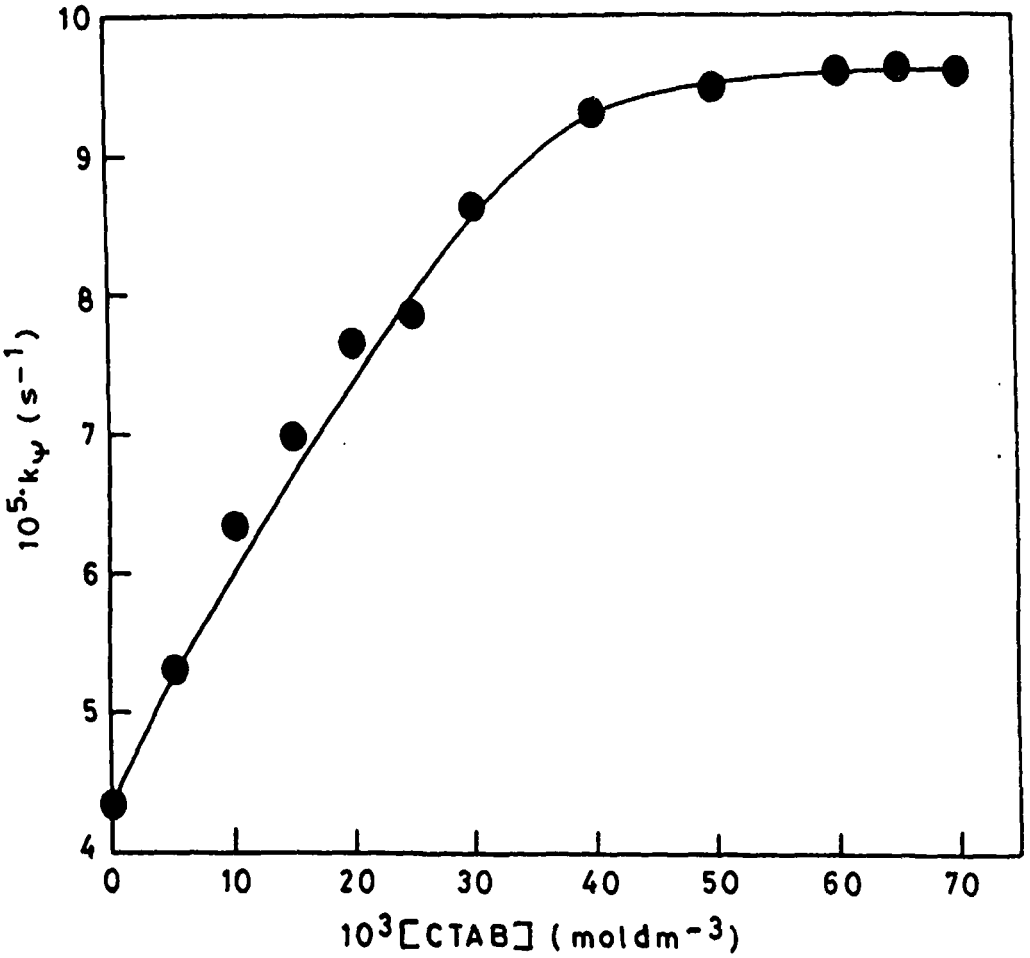


Fig. 5.4. k_ψ–[CTAB] profile. [L-isoleucine] =6.0x10^{-4} mol dm^{-3}, [ninhydrin] =10.0x10^{-3} mol dm^{-3}, pH =5.0, temp.=80 ^{0}C.

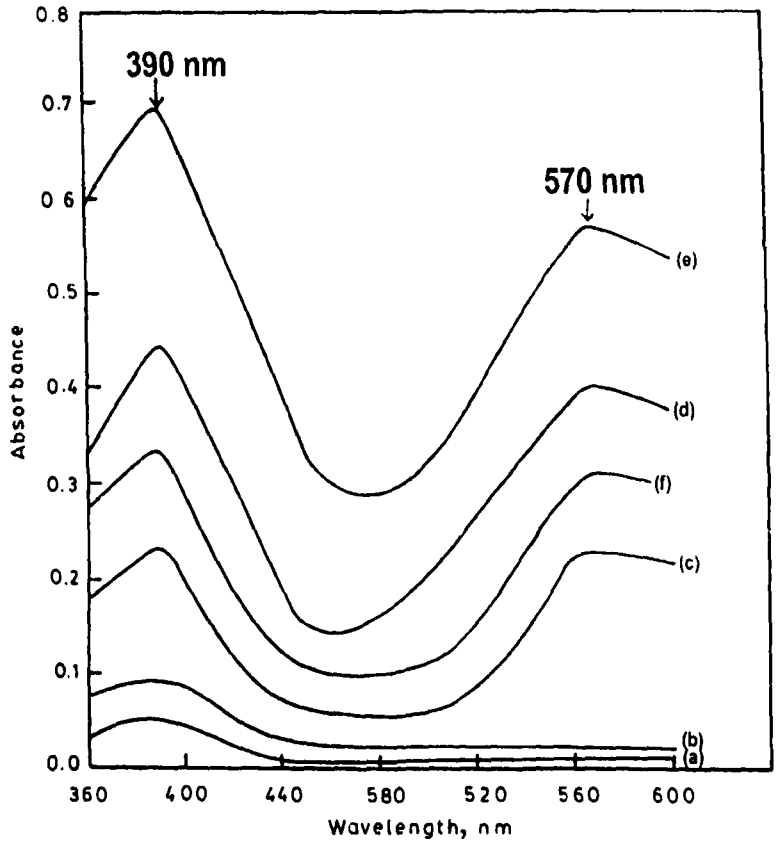


Fig. 5.5. Absorption spectra of the reaction product of L-isoleucine with ninhydrin in the absence and presence of surfactant. (a) after heating the reaction mixtures at 80 °C, (b) same as solution (a) in presence of [CTAB] = 20.0×10^{-5} mol dm^{-3}, (c) same as solution (a) in presence of [16-4-16] = 20.0×10^{-5} mol dm^{-3}, (d) after boiling solution (b), (e) after boiling solution (c), (f) same as solution (c) in presence of 10% DMSO. Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, pH = 5.0.

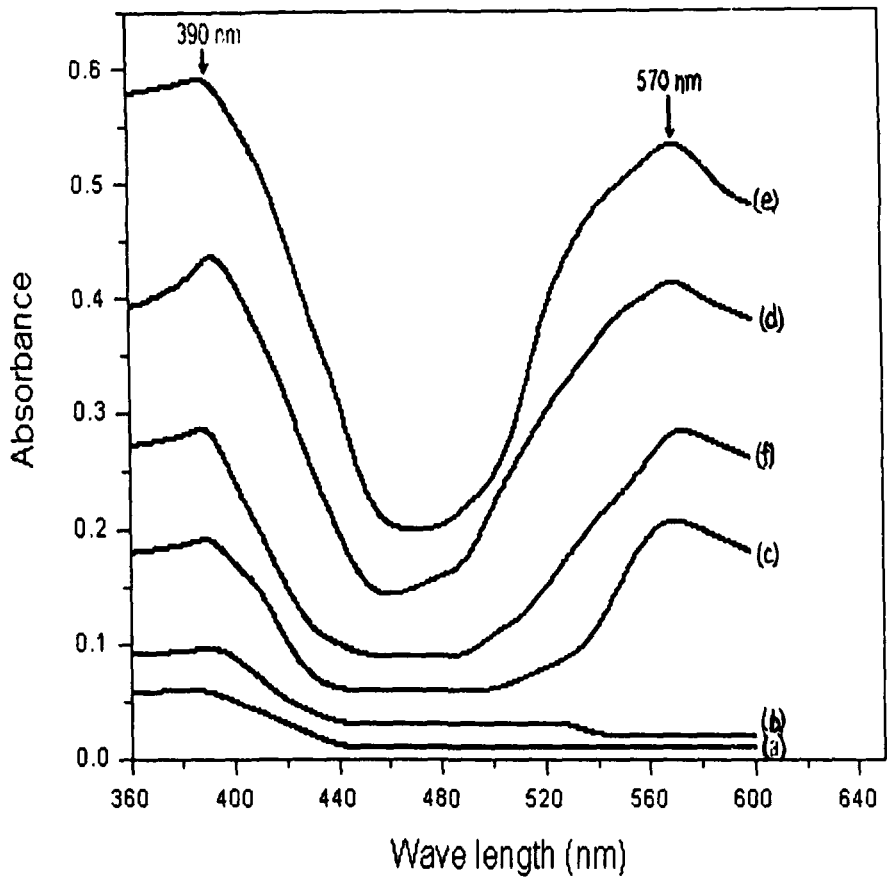


Fig. 5.6. Absorption spectra of the reaction product of L-isoleucine with ninhydrin in the absence and presence of surfactant. (a) after heating the reaction mixtures at 80 °C, (b) same as solution (a) in presence of [CTAB] = 20.0×10^{-5} mol dm^{-3}, (c) same as solution (a) in presence of [16-5-16] = 20.0×10^{-5} mol dm^{-3}, (d) after boiling solution (b), (e) after boiling solution (c), (f) same as solution (c) in presence of 10% DMSO. Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, pH = 5.0.

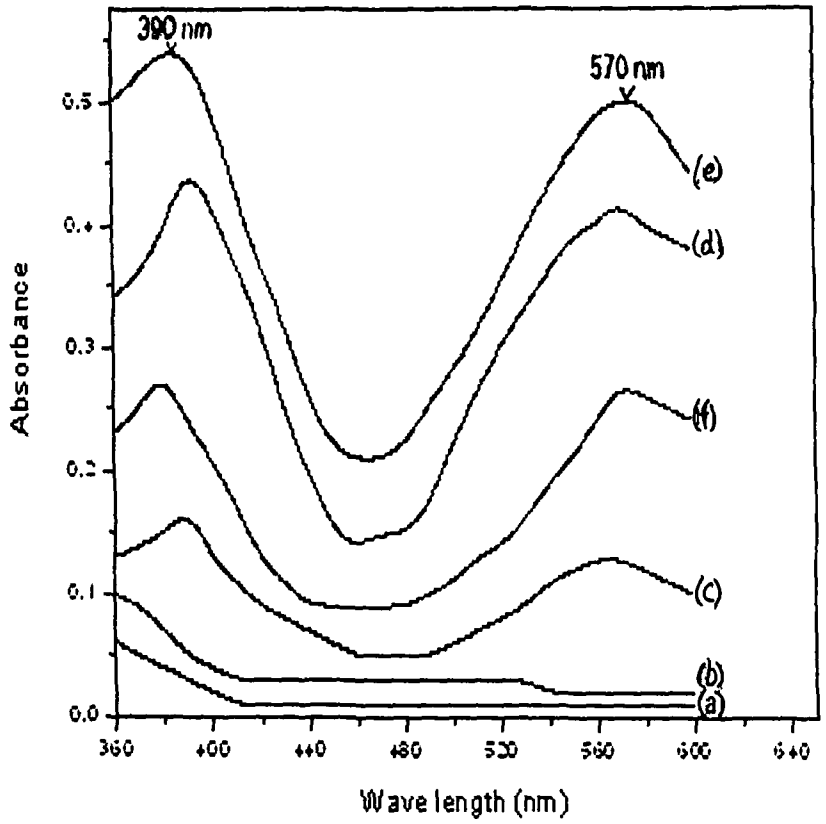


Fig. 5.7. Absorption spectra of the reaction product of L-isoleucine with ninhydrin in the absence and presence of surfactant. (a) after heating the reaction mixtures at 80 °C, (b) same as solution (a) in presence of [CTAB] = 20.0×10^{-5} mol dm^{-3}, (c) same as solution (a) in presence of [16-6-16] = 20.0×10^{-5} mol dm^{-3}, (d) after boiling solution (b), (e) after boiling solution (c), (f) same as solution (c) in presence of 10% DMSO. Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, pH = 5.0.

Table 5.4: Dependence of rate constants on pH, [L-isoleucine] and [ninhydrin] in the presence of gemini surfactants (=20.0x10^{-5} mol dm^{-3}) at 80 °C.

10^4[L-isoleucine] (mol dm^{-3})	10^3[ninhydrin] (mol dm^{-3})	pH	10^5 k_ψ (s^{-1})		
			16-4-16	*16-5-16*	*16-6-16*
1.0	5.0	3.5	2.6	1.8	0.9
1.0	5.0	4.0	3.0	2.0	1.0
1.0	5.0	4.5	3.5	2.3	1.1
1.0	5.0	5.0	7.9	6.4	4.6
1.0	5.0	5.5	8.3	6.6	4.8
1.0	5.0	6.0	8.4	7.1	5.3
1.0	5.0	5.0	7.9	6.4	4.6
1.5	5.0	5.0	7.6	6.9	4.8
2.0	5.0	5.0	7.8	6.9	5.0
2.5	5.0	5.0	7.8	6.9	4.5
3.0	5.0	5.0	8.0	7.0	4.8
3.5	5.0	5.0	7.7	6.9	4.9
1.0	5.0	5.0	7.9	6.4	4.6
1.0	10.0	5.0	18.4	14.3	11.3
1.0	15.0	5.0	29.7	23.2	20.4
1.0	20.0	5.0	39.4	31.9	26.7
1.0	25.0	5.0	48.0	38.6	34.5
1.0	30.0	5.0	53.0	44.6	37.6
1.0	35.0	5.0	57.2	49.3	40.4
1.0	40.0	5.0	60.2	52.1	43.5

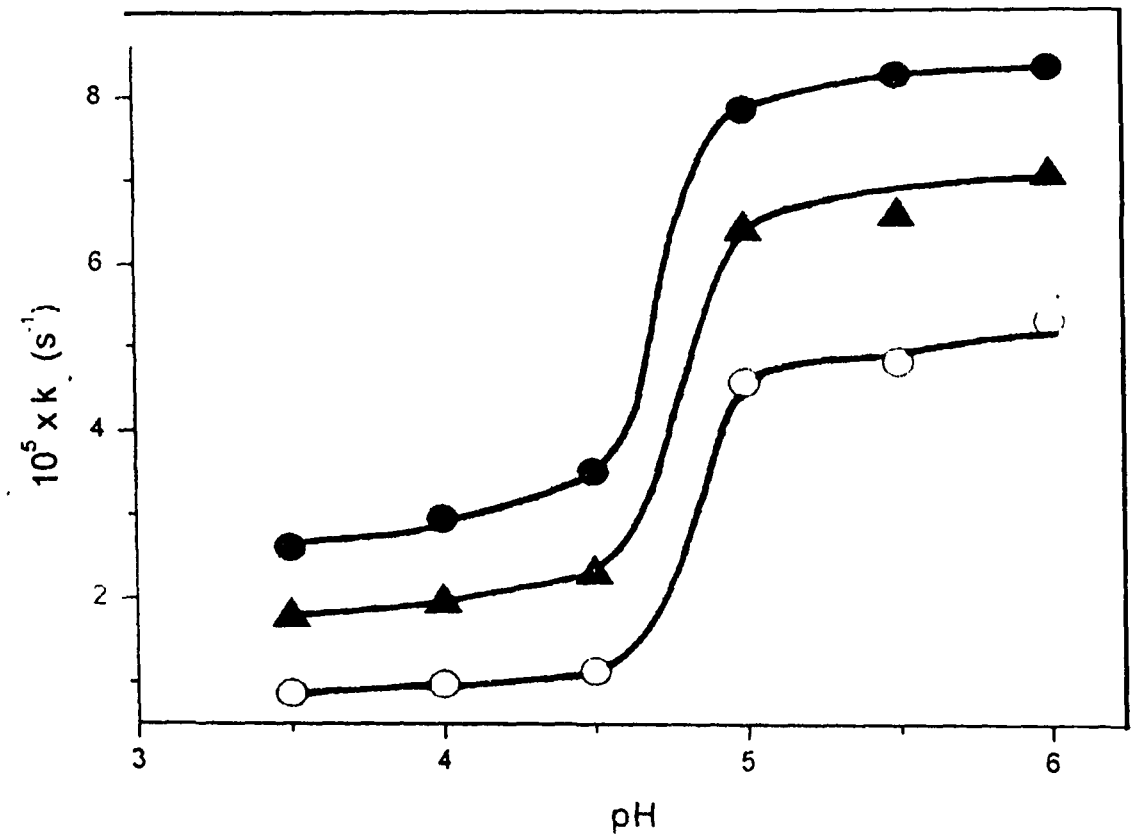


Fig. 5.8. k_ψ – pH profiles for the reaction of ninhydrin with L-isoleucine, 16-4-16 (●),16-5-16 (▲),16-6-16 (○). Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, [16-*s*-16] = 20.0×10^{-5} mol dm^{-3}, temp. = 80 °C.

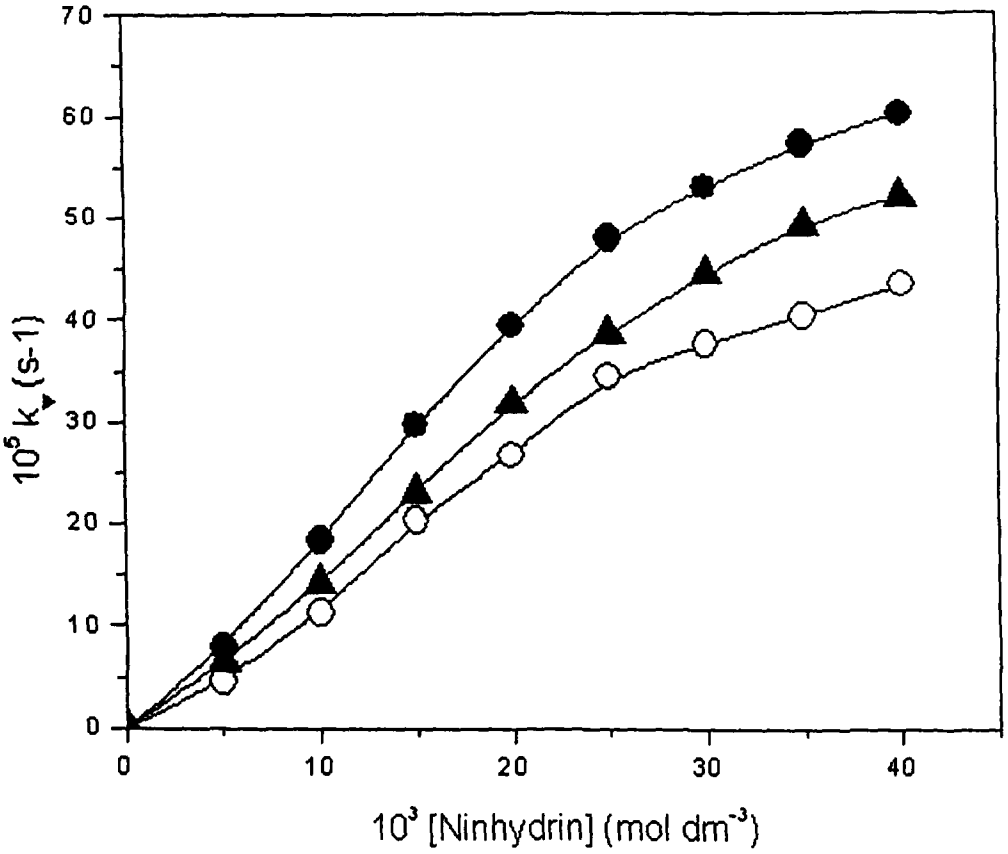


Fig. 5.9. Plots of k_ψ vs. [ninhydrin] for the reaction of ninhydrin with L-isoleucine, 16-4-16 (●),16-5-16 (▲),16-6-16 (○). Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [16-*s*-16] = 20.0×10^{-5} mol dm^{-3}, pH= 5.0, temp. =80 °C.

Table 5.5: Rate Constants for the reaction of ninhydrin (=5.0x10^{-3} mol dm^{-3}) with L-isoleucine (=1.0x10^{-4} mol dm^{-3}) in 16-6-16, 16-5-16, 16-4-16 micellar systems at constant pH (5.0) and temperature (80 °C).

10^5[surfactant] (mol dm^{-3})	16-6-16			16-5-16			16-4-16		
	$10^5 k_\psi$ (s^{-1})	$10^5 k_{\psi,cal}$ (s^{-1})	$\frac{k_\psi - k_{\psi,cal}}{k_\psi}$	$10^5 k_\psi$ (s^{-1})	$10^5 k_{\psi,cal}$ (s^{-1})	$\frac{k_\psi - k_{\psi,cal}}{k_\psi}$	$10^5 k_\psi$ (s^{-1})	$10^5 k_{\psi,cal}$ (s^{-1})	$\frac{k_\psi - k_{\psi,cal}}{k_\psi}$
1.0	1.9	-	-	2.8	-	-	3.6	-	-
3.0	3.3	-	-	4.1	-	-	4.7	-	-
5.0	3.8	-	-	4.5	-	-	5.5	-	-
8.0	4.4	-	-	4.9	-	-	6.0	6.0	+0.00
10.0	4.5	4.6	–0.02	5.5	5.5	+0.00	6.9	6.9	+0.00
20.0	4.6	4.6	+0.00	6.4	6.4	+0.00	7.9	7.9	+0.00
30.0	5.4	5.4	+0.00	6.7	6.7	+0.00	8.5	8.5	+0.00
50.0	5.6	5.6	+0.00	7.0	7.0	+0.00	8.8	8.8	+0.00
60.0	5.7	5.7	+0.00	7.2	7.2	+0.00	9.0	9.0	+0.00
80.0	5.8	5.8	+0.00	7.6	7.6	+0.00	-	-	-
90.0	5.8	5.8	+0.00	7.7	7.6	+0.01	9.5	9.5	+0.00
100.0	5.9	5.9	+0.00	7.7	7.7	+0.00	9.7	9.7	+0.00
250.0	6.4	6.3	+0.02	8.1	8.1	+0.00	10.1	10.1	+0.00
400.0	7.0	6.9	+0.01	8.3	8.3	+0.00	10.9	10.9	+0.00
500.0	7.2	7.2	+0.00	10.5	10.5	+0.00	14.2	14.2	+0.00

Contd...

1000.0	10.6	10.6	+0.00	12.1	12.2	–0.01	14.4	14.4	+0.00
1500.0	11.0	11.0	+0.00	12.4	12.4	+0.00	14.6	14.6	+0.00
2000.0	11.5	11.5	+0.00	13.0	13.0	+0.00	14.9	14.9	+0.00
2500.0	12.0	11.5	+0.04	13.2	13.2	+0.00	15.5	15.5	+0.00
3000.0	12.2	12.0	+0.02	13.7	13.7	+0.00	15.9	15.8	+0.01

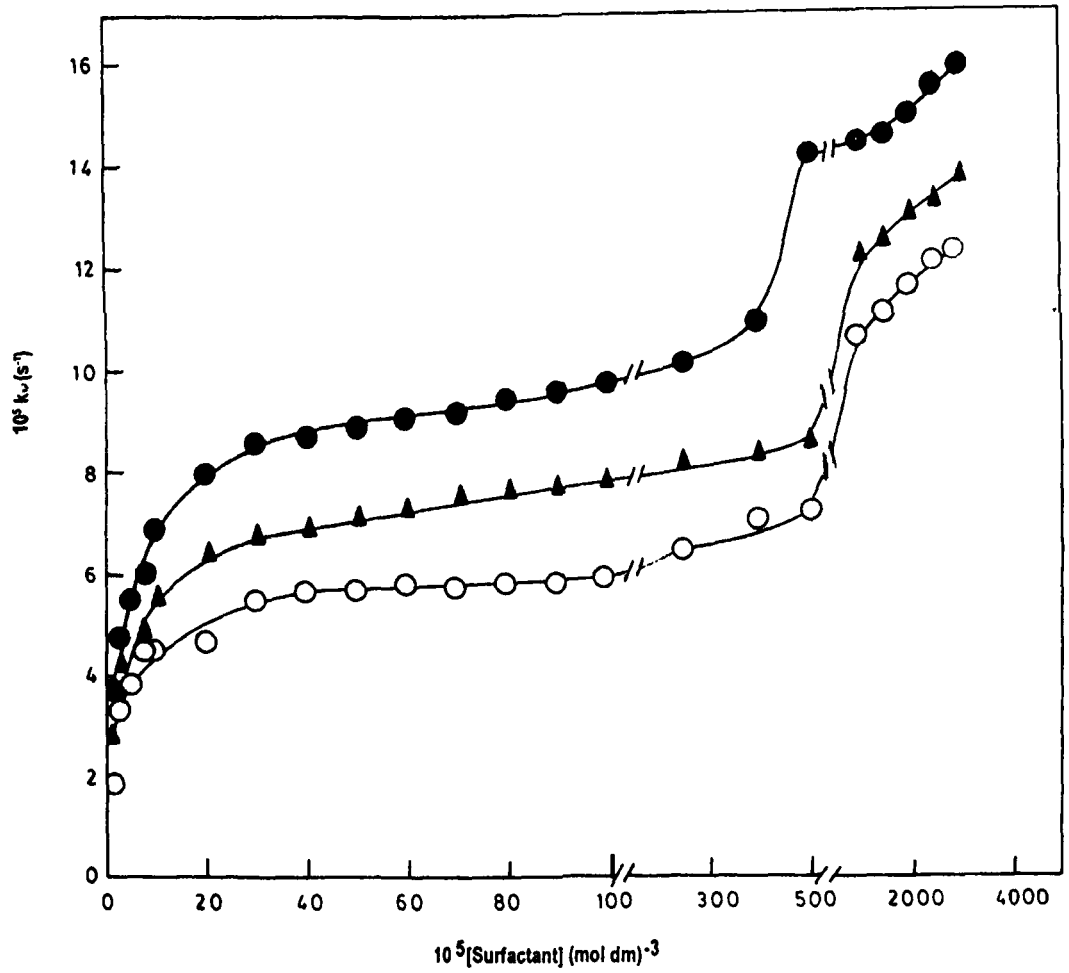


Fig. 5. 10. k_ψ – [surfactant] profiles for the reaction of ninhydrin with L-isoleucine, 16-4-16 (●),16-5-16 (▲),16-6-16 (○). Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, pH = 5.0, temp.= 80 °C.

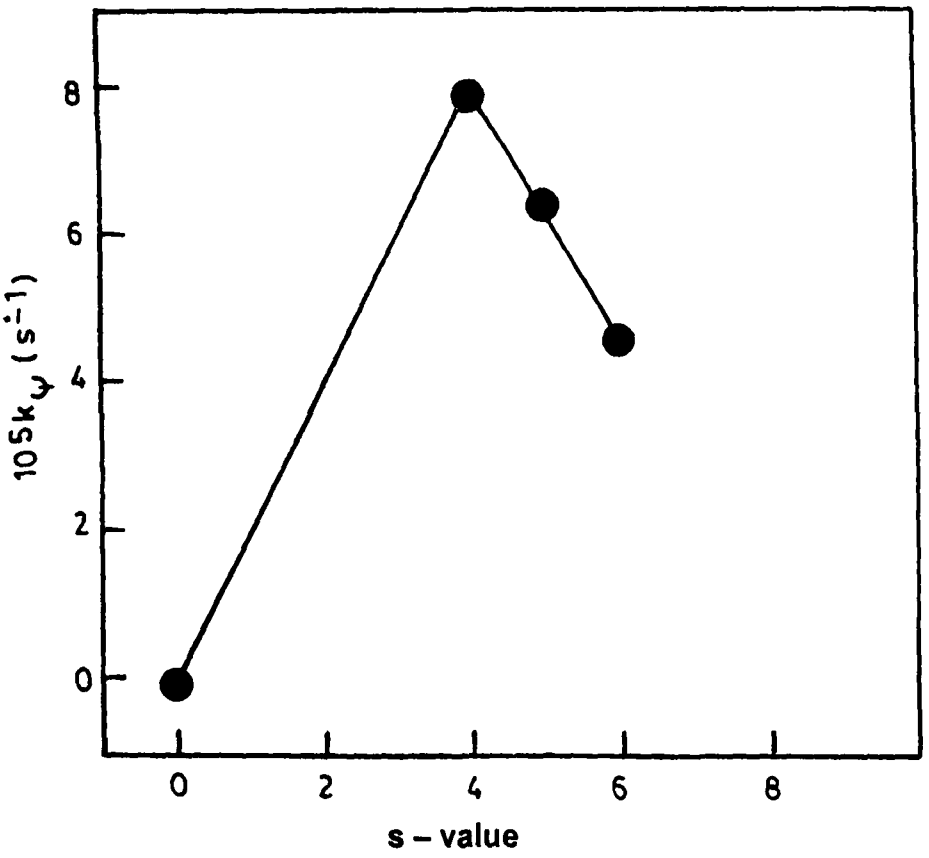


Fig. 5.11. Variation of k_ψ as a function of the spacer chain length (*s*-value) of 16-*s*-16 surfactants 20.0×10^{-5} mol dm^{-3}. Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, [surfactant]= 20.0×10^{-5} mol dm^{-3} pH = 5.0, temp. =80 °C. The corresponding k_ψ in CTAB micelles represents the point at the "*s*-value = 0".

Table 5.6: Values of line width at half-height signals (lw, Hz) for gemini surfactants 16-4-16, 16-5-16, 16-6-16 at concentrations below and above the transition to larger aggregates.[a]

	16-4-16		16-5-16		16-6-16	
	0.5mM	10mM	2.0mM	70mM	0.5mM	100mM
$-N^{+}CH_3$	36.01	48.62	25.21	54.02	30.61	54.02

[a] ^{1}HNMR spectra were recorded in D_2O at 25°C.

Table 5.7: Critical micelle concentration (cmc) values of CTAB and geminis determined by conductivity measurements in absence and presence of L- isoleucine and ninhydrin at 30 and 80 °C.

Solution	10^5 cmc (mol dm^{-3})	
	30 °C	80 °C
CTAB	100.0	170.0
CTAB + isoleuine[a]	99.0	165.0
CTAB + ninhydrin[a]	98.0	155.0
CTAB + isoleucine + ninhydrin[a]	101.0	160.0
16-4-16	2.8	7.1
16-4-16 + isoleucine[b]	2.7	6.9
16-4-16 + ninhydrin[b]	2.6	6.8
16-4-16 + isoleucine + ninhydrin[b]	2.8	7.0
16-5-16	3.6	8.4
16-5-16 + isoleucine[b]	3.5	8.1
16-5-16 + ninhydrin[b]	3.4	8.2
16-5-16 + isoleucine + ninhydrin[b]	3.7	8.3
16-6-16	4.4	9.6
16-6-16 + isoleucine[b]	4.1	9.2
16-6-16 + ninhydrin[b]	4.2	9.3
16-6-16 + isoleucine + ninhydrin[b]	4.3	9.4

[a] [L-isoleucine] = 6.0×10^{-4} mol dm^{-3}, [ninhydrin] = 10.0×10^{-3} mol dm^{-3}

[b] [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}

Table 5.8: Values of k'_m and binding constants (K_S, K_N) for the reaction of ninhydrin with L-isoleucine in presence of CTAB[a] (=40.0x10^{-3} mol dm^{-3})/ geminis[b] (=20.0x10^{-5} mol dm^{-3}) at 80 °C.

Parameter/Constant	CTAB[a]	16-4-16[b]	16-5-16[b]	16-6-16[b]
$10^2\ k'_m\ (s^{-1})$	0.072	1.37	1.96	5.82
$K_S\ (mol^{-1}dm^3)$	56.0	68.0	70.0	76.0
$K_N\ (mol^{-1}dm^3)$	79.6	73.44	68.25	65.38

[a] [L-isoleucine] = 6.0x10^{-4} mol dm^{-3}, [ninhydrin] = 10.0x10^{-3} mol dm^{-3})

[b] [L-isoleucine] = 1.0x10^{-4} mol dm^{-3}, [ninhydrin] = 5.0x10^{-3} mol dm^{-3})

Table 5.9: Effect of solvents on the rate constants (k_ψ) for the reaction of L-isoleucine (=1.0x10^{-4} mol dm^{-3}) with ninhydrin (=5.0x10^{-3} mol dm^{-3}) in the presence of 16-4-16 (=20.0X10^{-5} mol dm^{-3}) at 80 °C.

% Solvent (v/v)	10^5 k_ψ (s^{-1})			
	AN	DMSO	MC	PrOH
0	7.9	7.9	7.9	7.9
5	15.5	11.1	9.5	13.0
10	19.1	14.5	11.0	18.8
15	27.5	17.8	12.5	20.5
20	38.8	21.0	14.5	28.0
25	47.3	26.3	19.5	34.3
30	54.5	32.0	26.5	44.5
35	65.2	45.0	34.0	49.9
40	84.0	63.5	43.5	52.5

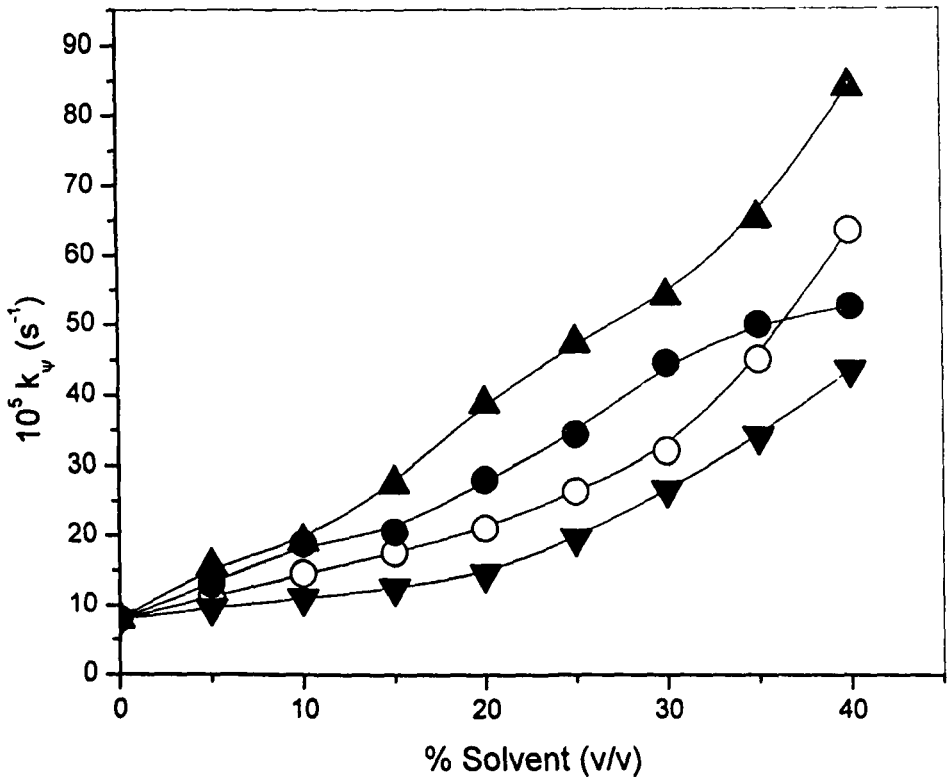


Fig. 5.12. Effect of methylcellosolve (▼), 1-propanol (●),dimethylsulfoxide (○) and acetonitrile (▲) on the reaction of ninhydrin with L-isoleucine. Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, [16-4-16] = 20.0×10^{-5} mol dm^{-3}, pH= 5.0, temp. = 80 °C.

Table 5.10: Effect of solvents on the rate constants (k_ψ) for the reaction of isoleucine (=1.0x10^{-4} mol dm^{-3}) with ninhydrin (=5.0x10^{-3} mol dm^{-3}) in the presence of 16-5-16 (=20.0X10^{-5} mol dm^{-3}) at 80 °C.

% Solvent (v/v)	$10^5 k_\psi$ (s^{-1})			
	AN	DMSO	MC	PrOH
0	6.4	6.4	6.4	6.4
5	11.5	8.0	6.5	10.0
10	17.0	11.0	7.5	15.0
15	24.0	13.5	9.0	19.0
20	31.5	17.0	10.5	24.5
25	39.5	22.5	14.0	30.0
30	50.5	28.0	23.0	38.0
35	63.0	34.0	37.5	46.5
40	79.0	44.0	53.0	55.5

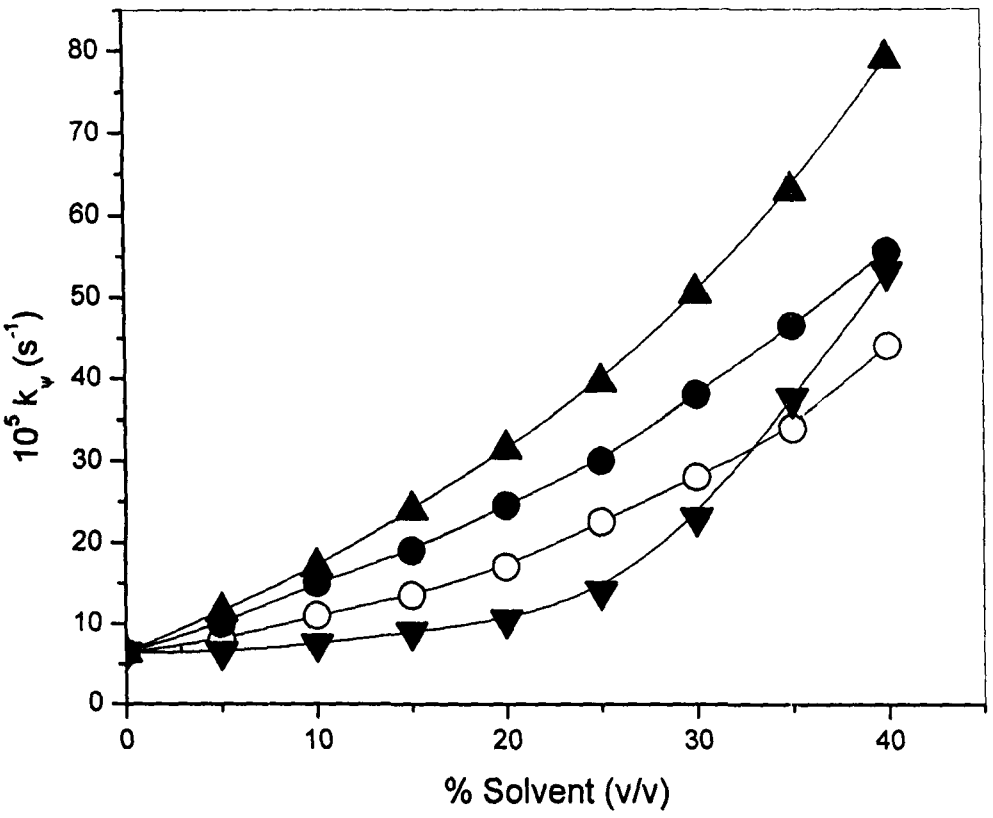


Fig. 5.13. Effect of methylcellosolve (▼), 1-propanol (●),dimethylsulfoxide (○) and acetonitrile (▲) on the reaction of ninhydrin with L-isoleucine. Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, [16-5-16] = 20.0×10^{-5} mol dm^{-3}, pH= 5.0, temp. = 80 °C.

Table 5.11: Effect of solvents on the rate constants (k_ψ) for the reaction of isoleucine (= $1.0x10^{-4}$ mol dm^{-3}) with ninhydrin (= $5.0x10^{-3}$ mol dm^{-3}) in the presence of 16-6-16 (= $20.0X10^{-5}$ mol dm^{-3}) at 80 °C.

% Solvent (v/v)	10^5 k_ψ (s^{-1})			
	AN	DMSO	MC	PrOH
0	4.6	4.6	4.6	4.6
5	10.5	6.0	5.0	8.0
10	15.5	8.0	6.0	11.5
15	21.0	10.5	8.0	16.0
20	27.5	13.0	9.5	20.0
25	34.5	15.5	12.5	25.0
30	42.5	19.0	17.0	30.0
35	51.0	23.0	29.0	35.0
40	62.5	30.0	44.0	40.0

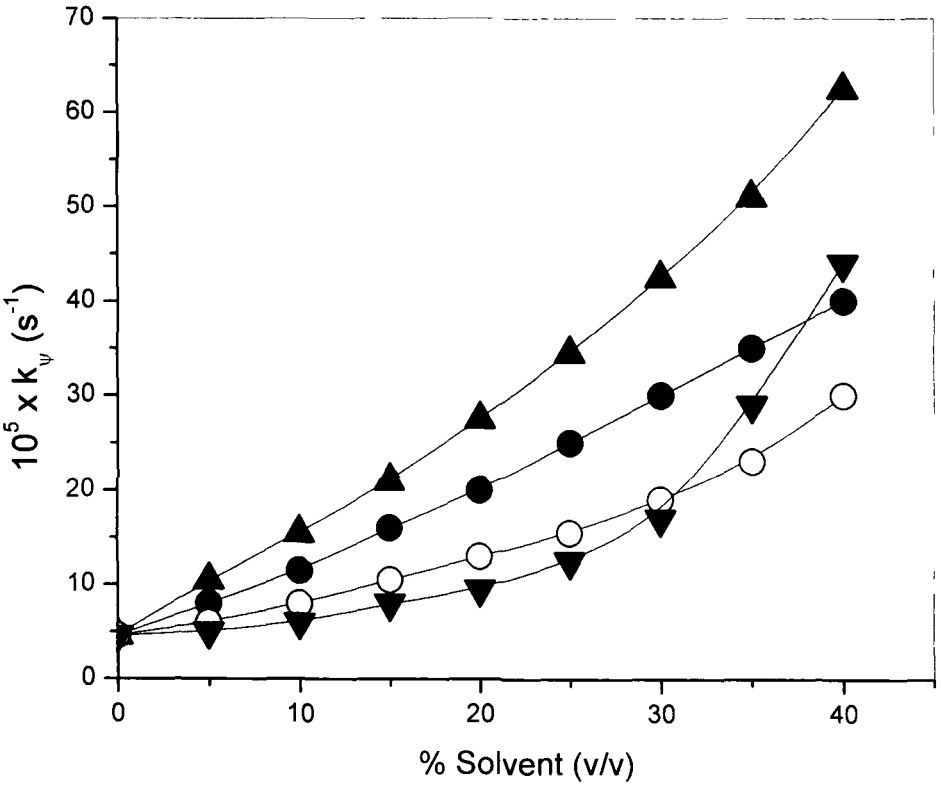


Fig. 5.14. Effect of methylcellosolve (▼),1-propanol (●), dimethylsulfoxide (○) and acetonitrile (▲) on the reaction of ninhydrin with L-isoleucine. Reaction conditions: [L-isoleucine] = 1.0×10^{-4} mol dm^{-3}, [ninhydrin] = 5.0×10^{-3} mol dm^{-3}, [16-6-16] = 20.0×10^{-5} mol dm^{-3}, pH= 5.0, temp. = 80 °C.

References

1. (a) D. J. McCaldin, *Chem. Rev.*, **60**, 39 (1960). (b) M. M. Joullie, T. R. Thompson and N. H. Nemeroff, *Tetrahedron*, **47**, 8791 (1991).
2. (a) S. Oden and B. Von Hofsten, *Nature*, **173**, 449 (1954). (b) J. Almog, "*Advances in Fingerprint Technology*", Edited by H. Lee and R. E. Gaensslen, Elsevier Science, New York (1991).
3. S. Ruhemann, *Trans. Chem. Soc.*, **97**, 1438 (1910); **99**, 1486 (1911).
4. (a) S. Moore, *J. Biol. Chem.*, **243**, 6281 (1968). (b) Z. Khan, M. Z. A. Rafiquee and A. A. Khan, *J. Indian Chem. Soc.*, **73**, 305 (1996).
5. (a) M. Friedman and C. W. Sigel, *Biochemistry*, **5**, 478 (1966). (b) P. J. Lamothe and P. G. McCormick, *Anal. Chem.*, **45**,1906 (1973).
6. (a) Z. Khan and A. A.Khan, *J. Indian Chem. Soc.*, **66**, 454 (1989). (b) Z. Khan and A. A.Khan, *J. Indian Chem. Soc.*, **67**, 463 (1990). (c) Z. Khan, S. I. Ali, M. Z. A Rafiquee and Kabir-ud-Din, *Indian J. Chem.*, **36A**, 579 (1997). (d) Kabir-ud-Din, M. Z. A. Rafiquee, M. Akram and Z. Khan, *Int. J. Chem. Kinet.*, **31**, 103 (1999). (e) Kabir-ud-Din, J. K. J. Salem, S. Kumar, M. Z. A. Rafiquee and Z. Khan, *J. Colloid. Interface Sci,* **215**, 9 (1999). (f) Kabir-ud-Din, J. K. J Salem, S. Kumar, M. Z. A.Rafiquee and Z. Khan, *Colloids Surf. A.*, **168**, 241 (2000). (g) Kabir-ud-Din, J. K. J. Salem, S. Kumar and Z. Khan,

Colloid. Surf. A, **168**, 241 (2000). (h) Kabir-ud-Din, J. K. J. Salem, S. Kumar and Z. Khan, *Indian J. Chem.*, **39A**, 1019 (2000). (i) Kabir-ud-Din, M. Bano and I. A. Khan, *J. Surface Sci. Technol.,* **18**, 113 (2002). (j) Kabir-ud-Din, M. Bano and I. A. Khan, *Indian J. Chem.*, **42A**, 998 (2003). (k) Kabir-ud-Din, M. Bano and I. A. Khan, *Indian J. Chem.*, **42B**, 1132 (2003). (l) Kabir-ud-Din, M. Bano and I. A. Khan, *J. Indian Chem. Soc.* **81**, 1111 (2004). (m) Kabir-ud-Din, W. Fatma and Z. Khan, *Int. J. Chem. Kinet.* **38**, 6342 (2006).

7. (a) T. Kunitake and T. Shinkai, *Adv. Phys. Org. Chem.*, **17**, 435 (1980). (b) J. H. Fendler, "*Membrane Mimetic Chemistry*", Wiley, New York (1981). (c) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, **22**, 213 (1986). (d) C. A. Bunton, F. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res.*, **24**, 357 (1991). (e) L. S. Romsted, C. A. Bunton and J. Yao, *Curr. Opin. Colloid Interface Sci.*, **2**, 622 (1997). (f) O. A. El Seoud, *Adv. Colloid Interface Sci.*, **30**, 1 (1989). (g) S. Tascioglu, *Tetrahedron*, **34**, 11113 (1996).
8. (a) "*CRC Handbook of Chemistry and Physic*", Edited by R. C. Weast, CRC Press Inc., Florida, 58th ed., (1977-1978). (b) R. C. Friedman and J. S. Wall, *J. Am. Chem. Soc.*, **86**, 3735 (1964).

9. J. D. Roberts and M. C. Caserio, "*Basic Principles of Organic Chemistry*", Benjamin, New York (1977).

10. F. M. Menger, C. E. Portnoy, *J. Am. Chem. Soc.*, **89**, 4698 (1967).

11. (a) C. A. Bunton, *Cat. Rev. Sci. Eng.*, **20**, 1 (1979). (b) C. A. Bunton, "*Surfactants in Solutions*", Edited by K. L. Mittal and D. O. Shah, Plenum Press, New York, Vol. 11 (1991). (c) C. A. Bunton, *J. Mol. Liq.*, **72**, 231 (1997).

12. S. Vera and E. Rodenas, *Tetrahedron*, **42**, 143 (1986).

13. T. J. Broxton and S. Wright, *J. Org. Chem.*, **51**, 2965 (1986).

14. G. Savelli, R. Germani and L. Brinchi, "*Reactions and Synthesis in Surfactant Systems*", Edited by J. Texter, Marcel Dekker: New York, p 175 (2001).

15. Kabir-ud-Din and Waseefa Fatma, *J. Phys. Org. Chem.*, (communicated).

16. L Brinchi, R. Germani, L. Goracci, G. Savelli and C. A. Bunton, **18**, 7821 (2002).

17.(a) J. Ulmius and H. J. Wennerstrom, *Magn. Reson.*, **28**, 309 (1977). (b) G. Cerichelli, L. Luchetti, G. Mancini and G. Savelli, *Langmuir*, **15**, 2631 (1999). (c) C. Groth, M. Nyden, K. Holmberg, J. R Kanicky and D. O. Shah, *J. Surf. Deterg.*, **7**, 247 (2004).

18.(a) R. Zana and Y. Talmon, *Nature*, **362**, 228 (1993). (b) R. Zana, *J. Colloid Interface Sci.*, **248**, 203 (2002).

19. S. De, V. K. Aswal, P. S. Goyal and S. Bhattacharya, *J. Phys. Chem.*, **100**, 11664 (1996).

20.C. A. Bunton, L-H. Gan, J. R. Moffatt, L. S. Romsted and G. Savelli, *J. Phys. Chem.*, **85**, 4118 (1981).

21. L. G. Ionescu, L. S. Romanesco and F. Nome, " *Surfactants in Solution*", Edited by K. L. Mittal and B. Lindman, Plenum Press, New York, Vol. 2 (1984).

22. M. Friedman, *J. Am. Chem. Soc.*, **89**, 4709 (1967).

23. E. H. Cordes, *Pure Appl. Chem.*, **50**, 617 (1978).

24. E. H. Cordes and R. B. Dunlap, *Acc. Chem. Res.*, **2**, 329 (1968).